Superconductivity and upper fields in Na-doped iron arsenides $\text{Eu}_{1-x}\text{Na}_x\text{Fe}_2\text{As}_2$

Yanpeng Qi, Lei Wang, Zhaoshun Gao, Xianping Zhang, Dongliang Wang, Chao Yao, Chunlei Wang, Chengduo Wang and Yanwei Ma$^1$

Key Laboratory of Applied Superconductivity, Institute of Electrical Engineering, Chinese Academy of Sciences, PO Box 2703, Beijing 100190, People’s Republic of China
E-mail: ywma@mail.iee.ac.cn

New Journal of Physics 14 (2012) 033011 (11pp)
Received 20 July 2011
Published 12 March 2012
Online at http://www.njp.org/
doi:10.1088/1367-2630/14/3/033011

Abstract. In this paper, we report a systematic investigation of the crystal structure and superconducting properties of iron-based superconductors $\text{Eu}_{1-x}\text{Na}_x\text{Fe}_2\text{As}_2$ ($x = 0–0.5$). X-ray diffraction patterns indicate that the compounds form the ThCr$_2$Si$_2$-type structure with space group I4/mmm. The systematic evolution of the lattice constant demonstrates that the Eu ions are successfully replaced by Na. The use of alkali metal substitution into the Eu site allows us to suppress the magnetic/structural phase transition in the parent compounds and superconductivity reaches as high as 35 K with a doping level of $x = 0.5$. In addition, single crystals of $\text{Eu}_{1-x}\text{Na}_x\text{Fe}_2\text{As}_2$ ($x = 0, 0.5$) have been successfully synthesized using the self-flux method. The upper critical fields have been determined with the magnetic field along the $ab$-plane and the $c$-axis, yielding an anisotropy of 1.7. The high upper critical fields and the low superconducting anisotropy of the Na-doped $\text{EuFe}_2\text{As}_2$ compounds indicate a potential for applications such as the generation of high magnetic fields.

$^1$ Author to whom any correspondence should be addressed.
1. Introduction

The recent discovery by Hosono et al [1] of superconductivity in electron-doped LaFeAsO$_{1-x}$F$_x$ at 26 K has ushered in a new era of high-temperature superconductivity. Among the various members of the iron-containing pnictides are four main families of materials, which show superconducting transitions upon substitution by a dopant or upon applying external pressure. They are (i) the quaternary ‘1111’ compounds $R$FeAsO, where $R$ represents a lanthanide such as La, Ce, Sm, etc, with transition temperatures as high as 56 K [1–6]; (ii) the ternary $A$Fe$_2$As$_2$ ($A$ = Ca, Sr, Ba, Eu) systems, also known as ‘122’ systems, which exhibit superconductivity up to 38 K [7–11]; (iii) the ‘111’ compounds LiFeAs with $T_c$ ~ 18 K [12–14]; and (iv) the binary chalcogenide ‘11’ system (e.g., FeSe) with superconducting transition temperatures up to 14 K [15]. The 122 system has received special attention and provides us with a great opportunity to investigate the intrinsic physical properties since large-scale crystals can be grown.

Since the discovery of iron-based superconductors, a great deal of effort has been devoted to studying the interplay between superconductivity and magnetism. EuFe$_2$As$_2$ is a unique member of the iron arsenide parent compound with ThCr$_2$Si$_2$-type structure [16], which shows an antiferromagnetic transition of Eu$^{2+}$ ions at a relatively high temperature of 20 K [17]. The interaction between magnetic moments of Fe$^{2+}$ and Eu$^{2+}$ may lead to rich physical phenomena. In addition, similar to (Ba, Sr) Fe$_2$As$_2$, the undoped EuFe$_2$As$_2$ compounds exhibit a clear anomaly in resistivity near 200 K [18, 19], which suggests that superconductivity may be realized by appropriate doping [10, 11, 20]. Recently we have reported high-temperature superconductivity in Eu$_{0.7}$Na$_{0.3}$Fe$_2$As$_2$, in which Na doping suppresses the spin-density wave (SDW) transition and in turn gives rise to superconductivity up to 34 K [21]. In this paper, we report a systematic investigation of the crystal structure and superconducting properties of Eu$_{1-x}$Na$_x$Fe$_2$As$_2$ ($x = 0–0.5$). X-ray diffraction patterns indicate that the compounds have formed the ThCr$_2$Si$_2$-type structure with a space group I4/mmm. The systematic evolution of the lattice constants demonstrates a successful chemical substitution. Na doping strongly weakens the anomaly and induces superconductivity up to 35 K. In addition, we have synthesized the superconducting Eu$_{1-x}$Na$_x$Fe$_2$As$_2$ single crystals. A high upper critical field of 120 T was obtained. The anisotropy of the Eu$_{0.5}$Na$_{0.5}$Fe$_2$As$_2$ superconductor was ~ 1.7. Both the high upper critical field and comparably low anisotropy are advantageous for applications under a high magnetic field.

2. Experimental

Polycrystalline samples were synthesized by using the one-step solid state reaction method. Details of the fabrication process are described elsewhere [21]. A stoichiometric mixture of
Eu filings, Fe powder, As chips and Na pieces was ground by using a ball milling method in Ar atmosphere for more than 15 h. In order to compensate for the loss of elements during the milling and sintering procedures, an extra 10% As and 10% Na were added. The raw powder was encased and sealed into Nb tubes. Finally, the samples were slowly heated to 850 °C for 35 h. Argon gas was allowed to flow into the furnace during the heat treatment process to reduce the oxidation of the samples. To obtain samples with better crystallinity, we tried to grow single crystals by the FeAs self-flux method [22–24]. FeAs precursor was synthesized by the reaction of Fe powder and As chips at 500 °C for 10 h and then at 700 °C for 20 h in a sealed Nb tube. Appropriate amounts of the starting materials of Eu, Na and FeAs were placed in an alumina crucible and sealed in an arc-welded pure iron tube. Samples were heated up to 1180 °C over 12 h, held at 1180 °C for 5–10 h, and then cooled slowly to 1030 °C (3–5 °C h⁻¹) and then more rapidly to room temperature.

Phase identification and crystal structure investigation were carried out by x-ray diffraction (XRD) using Cu $K_\alpha$ radiation from 10° to 80°. The analysis of x-ray diffraction data was done and the lattice constants were derived. The crystal surface morphology and composition were examined by scanning electron microscopy (SEM) and energy-dispersive x-ray (EDX) analysis. Resistivity measurements were performed by the conventional four-point-probe method using a Quantum Design physical property measurement system (PPMS) with magnetic field up to 9 T. Ac magnetic susceptibility of the samples was measured by an Oxford cryogenic system (Maglab-12).

3. Results and discussion

In order to have a comprehensive understanding of the evolution induced by the doping process, we measured the x-ray diffraction patterns for all samples. Figure 1 shows the XRD patterns of Eu$_{1-x}$Na$_x$Fe$_2$As$_2$ samples ($x = 0–0.5$). All the main peaks of samples can be indexed to the tetragonal structure very well, indicating that the samples are essentially single phase. Small amounts of impurity phases, mostly perhaps FeAs, were also observed in the XRD patterns. Such tiny amounts of second phase, together with the granular behavior of the samples, may influence the zero resistance point, but do not obviously influence the upper critical field and the normal state properties. By fitting the XRD data to the structure with the software X’Pert Plus, we obtain the lattice constants of Eu$_{1-x}$Na$_x$Fe$_2$As$_2$ ($x = 0–0.5$). In figure 2, the $a$-axis and $c$-axis lattice parameters for Eu$_{1-x}$Na$_x$Fe$_2$As$_2$ samples are shown. In the parent phase EuFe$_2$As$_2$, the lattice constants are $a = 0.3908$ nm and $c = 1.2144$ nm, which are in agreement with previous reports [18]. It is clear that by substituting the Na into the Eu site, the $a$-axis lattice constant shrinks, whereas the $c$-axis one expands. This tendency is similar to the case of doping potassium to the site of A in A$_{1-x}$K$_x$Fe$_2$As$_2$ (A = Ba, Sr) [7, 8], or substituting Ca with Na in Ca$_{1-x}$Na$_x$Fe$_2$As$_2$ [9]. The nearly linear variation in the lattice parameters indicates successful chemical substitution.

In figure 3, we present the temperature dependence of electrical resistivity for Eu$_{1-x}$Na$_x$Fe$_2$As$_2$ samples with $x = 0–0.5$. Data normalized by the room temperature resistivity $R_{300K}$ are shown to remove uncertainty in estimation of the absolute value due to geometric factors. Successive data sets are offset vertically by 1 for clarity. The Mossbauer study indicated that EuFe$_2$As$_2$ experienced two magnetic transitions: the iron sublattice and europium sublattice are respectively ordered antiferromagnetically near 200 and 18 K [17]. From the $\rho$–$T$ curve, we can easily observe two anomalies. Except for a small kink at about 20 K related to the AFM
ordering of Eu$^{2+}$ ions, the parent EuFe$_2$As$_2$ compound also exhibits a resistivity anomaly at about 185 K, which is associated with the magnetic/structural phase transition [18, 19]. Na doping leads to suppression of the anomaly obviously in resistivity. The curve for the sample with $x = 0.1$ shows a small but clear anomaly on passing through the temperature of the coupled structural/magnetic transition $T_{an} \sim 160$ K, with resistivity accelerating its decrease on cooling. The minimum distinct value of $T_{an} \sim 120$ K is observed in Eu$_{0.8}$Na$_{0.2}$Fe$_2$As$_2$ samples with
Figure 3. Temperature dependence of resistivity for the polycrystalline samples Eu$_{1-x}$Na$_x$Fe$_2$As$_2$ ($x = 0$–0.5) measured in zero field. The data are normalized to $R_{300K}$.

Figure 4. Temperature dependence of ac magnetization for Eu$_{0.5}$Na$_{0.5}$Fe$_2$As$_2$. The measurements were done with $H_{ac} = 0.1$ Oe and $f = 333$ Hz. The correlated drop in resistivity for the nominal $x = 0.5$ sample is also shown in the figure.

$T_c = 8$ K. In the sample of $x = 0.3$, the superconducting critical temperature $T_c$ was observed up to 20 K. With a further increase in Na fraction to $x = 0.5$, the maximal $T_c$ at 35 K was found. The residual resistivity ratio $RRR = \rho(300 \text{ K})/\rho(35 \text{ K}) = 7.35$, which is consistent with that of the Ba$_{1-x}$K$_x$Fe$_2$As$_2$ sample [7].

To further confirm the superconductivity of Eu$_{1-x}$Na$_x$Fe$_2$As$_2$ samples, ac magnetic susceptibility measurements are also performed. Figure 4 shows the temperature dependence of ac magnetization for the Eu$_{0.5}$Na$_{0.5}$Fe$_2$As$_2$ sample. The correlated drop in resistivity for the
Figure 5. Temperature dependence of resistivity for the polycrystalline samples Eu$_{0.5}$Na$_{0.5}$Fe$_2$As$_2$ at different magnetic fields. Inset: the upper critical field $H_{c2}$ and $H_{irr}$ as a function of temperature for Eu$_{0.5}$Na$_{0.5}$Fe$_2$As$_2$. The same sample is also shown in the figure. The measurements were carried out with a frequency of 333 Hz and an amplitude of 0.1 Oe. The onset magnetic transition point was determined as the drop of $\chi'$. The sample shows a good diamagnetic signal and superconductivity with $T_c = 33.5\, \text{K}$, which corresponds to the middle transition point of resistance. Estimation on the magnetic signal indicates that the superconducting shielding volume of the sample is beyond 90%. From the $\rho$–$T$ curve, we observe that the transition width $\Delta T$ is $\sim 1.2\, \text{K}$. The diamagnetism and presence of zero resistance in the samples are proof that Na substitution in the EuFe$_2$As$_2$ compound leads to superconductivity.

The temperature dependence of resistivity under different magnetic fields is presented in figure 5. Like many other iron-pnictide superconductors, the superconductivity is very robust against the magnetic field, and both onset transition point and zero resistance point shift to lower temperatures. We used the criterion of 90 and 10% $\rho_n$ to estimate the upper critical field ($H_{c2}$) and irreversibility field ($H_{irr}$), and show the data in the inset of figure 5. It is clear that the curve of $H_{c2} (T)$ is very steep with a slope of $-dH_{c2}/dT|_{T_c} = 3.93\, \text{T/K}$. The value is rather large, which indicates a high upper critical field in this system. In order to estimate the upper critical field in the low-temperature region, we adopted the Werthamer–Helfand–Hohenberg formula [25] $H_{c2}(0) = 0.693 \times (dH_{c2}/dT) \times T_c$. Taking $T_c = 34.5\, \text{K}$, we get $H_{c2}(0) \approx 95\, \text{T}$. It is clear that the irreversibility field is rather high compared to that in MgB$_2$. It should be noted that this is a very rough estimation of the irreversibility line. According to the relationship between $H_{c2}$ and the coherence length $\xi$, namely, $H_{c2} = \Phi_0/(2\pi \xi^2)$, where $\Phi_0$ is the flux quantum, the value of the coherence length is estimated to be $\sim 18\, \text{Å}$ ($H_{c2}(0) \approx 95\, \text{T}$).

Based on the measurements described above, we can establish a composition–temperature phase diagram for Eu$_{1-x}$Na$_x$Fe$_2$As$_2$, shown in figure 6. Both $T_{an}$ and $T_c$ were defined as the temperature at which the anomaly appears in resistivity and the superconducting transition, respectively. Na doping suppresses the magnetic/structural phase transition in the undoped parent compound, the superconducting state emerges at $x = 0.2$, and the highest $T_c \sim 35\, \text{K}$. 

New Journal of Physics 14 (2012) 033011 (http://www.njp.org/)
was observed at $x = 0.5$. It should be noted that superconductivity emerges over a finite compositional range and coexists with AFM order over an even more limited range of Na doping. However, here it is impossible to know whether the coexistence between magnetism and superconductivity occurs at the atomic scale or comes from phase segregation, and further studies at the microscopic level are needed to assess this point.

In order to obtain samples with better crystallinity, we tried to grow single crystals by the flux method [22–24]. By controlling the content of Na, we obtained two kinds of crystal: undoped parent sample and superconducting samples. The as-grown crystals all have very shiny plate-like cleaved surfaces. Because the real contents of each element always deviate from the starting material in the flux method, the actual chemical composition of our single crystals was determined by EDX analysis. Typical EDX spectra are shown in figure 7. The actual atomic ratios are very close to the stoichiometric compound of Eu$_{1-x}$Na$_x$Fe$_2$As$_2$ ($x = 0$ and 0.5).

The crystal structure of as-grown samples was examined by x-ray diffraction measurement with the incident x-ray along the c-axis. Typical diffraction patterns are shown in figure 8. Only sharp peaks along (00l) could be observed, indicating high c-axis orientation and crystalline quality in our samples. A clear shift for each peak shows up, which indicates that the lattice has a little variation after doping Na into the parent phase. The raw data of XRD were analyzed by Powder X software [26] and the c-axis parameters were calculated. The lattice parameter values are $c = 1.2178$ nm for undoped EuFe$_2$As$_2$ compound and $c = 1.2336$ nm for Eu$_{0.5}$Na$_{0.5}$Fe$_2$As$_2$ compound, which are consistent with that of polycrystalline samples.

Figure 9 shows the temperature dependence of the in-plane electrical resistivity for Eu$_{1-x}$Na$_x$Fe$_2$As$_2$ samples with $x = 0$ and 0.5, respectively. For the parent compound, two strong anomalies show up at 185 and 20 K respectively, similar to the polycrystalline samples. It should be noted that $\rho(T)$ shows a slight upturn, leading to a peak before decreasing rapidly with further reduction of temperature. The increase in resistivity may be attributed to the opening of a gap at the Fermi surface due to the formation of the SDW [19]. In addition, the resistivity upturn has not been observed in polycrystalline samples, which implies an anisotropic temperature

Figure 6. Phase diagram of Eu$_{1-x}$Na$_x$Fe$_2$As$_2$ within the range $0 \leq x \leq 0.5$. Both $T_c$ and $T_{an}$ are determined by resistivity.
dependence of the resistivity at about $T_{an}$. In the Na-doped Eu$_{0.5}$Na$_{0.5}$Fe$_2$As$_2$ sample, the high-temperature anomaly is suppressed and then superconductivity at $\sim 35$ K occurs. The transition width is $\sim 0.5$ K, indicating the good quality of our samples. It should be noted that the anomaly is not completely suppressed and a slight bump around 160 K is also observed in the $\rho$--$T$ curve. Thus further experiment is needed for the interpretation: either the coexistence
Figure 9. Temperature dependence of resistivity for the single crystal Eu$_{1-x}$Na$_x$Fe$_2$As$_2$ ($x = 0$ and 0.5) measured in zero field. The data are normalized to $R_{300K}$.

Figure 10. (a, b) show the temperature dependence of resistivity for the single crystal Eu$_{0.5}$Na$_{0.5}$Fe$_2$As$_2$ with the magnetic field perpendicular and parallel to the $c$-axis, respectively.

of superconductivity and magnetism or the presence of phase separation in the Na-doped Eu122 system.

Resistivity as a function of temperature under the magnetic field applied in the $ab$-plane and along the $c$-axis is shown in figures 10(a) and (b). The transition temperature of superconductivity is suppressed gradually; however, obvious differences for the effect of field along different directions on the superconductivity can be observed. To discuss the anisotropy of superconductivity precisely, we tried to estimate the upper critical field ($H_{c2}$) and irreversibility field ($H_{irr}$) using the 90% and 10% points on the resistive transition curves. The estimated upper critical field ($H_{c2}$) and irreversible field ($H_{irr}$) are plotted in figures 11(a)
Figure 11. (a, b) show the temperature dependence of $H_{c2}$ and $H_{irr}$ for the single crystal Eu$_{0.5}$Na$_{0.5}$Fe$_2$As$_2$.

and (b), respectively. The upper critical fields $H_{c2}(T)$ exhibit a rather linear temperature dependence for both orientations. Using the Werthamer–Helfand–Hohenberg formula \[ H_{c2}(0) = 0.693 \times (dH_{c2}/dT) \times T_c, \] we can estimate the values of the upper critical fields: $H_{c2}^{ab} = 120\, \text{T}$ and $H_{c2}^{c} = 69.5\, \text{T}$. The anisotropy parameter, $H_{c2}^{ab}/H_{c2}^{c}$, is estimated to be $\sim 1.7$, which is consistent with the value of 1.70–1.84 in Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ [27]. Compared to the anisotropy in other iron-based superconductors, such as 5 in NdFeAsO$_{1-x}$F$_x$ [28], 3.0–3.6 in A$_x$Fe$_2$Se$_2$ [29, 30], these values are all quite small compared to high-$T_c$ cuprates. The high upper critical field and comparably low anisotropy are advantageous for applications in high-field magnets.

4. Conclusions

In summary, we have synthesized a series of layered Eu$_{1-x}$Na$_x$Fe$_2$As$_2$ ($x = 0–0.5$) compounds using one-step solid state reaction method, which crystallizes in ThCr$_2$Si$_2$-type structure with space group I4/mmm. The systematic evolution of the lattice constants indicates successful chemical substitution. The diamagnetism and presence of zero resistance in the samples are proof that Na substitution in the EuFe$_2$As$_2$ compounds leads to superconductivity. In addition, we also synthesized Eu$_{1-x}$Na$_x$Fe$_2$As$_2$ single crystals by the FeAs self-flux method. A high upper critical field of 120 T was obtained. The anisotropy of the Eu$_{0.5}$Na$_{0.5}$Fe$_2$As$_2$ superconductor determined by the ratio of $H_{c2}^{ab}$ and $H_{c2}^{c}$ is estimated as 1.7. Both the high upper critical field and comparably low anisotropy are advantageous for applications under a high magnetic field.

Acknowledgments

The authors thank Professors Haihu Wen, Liye Xiao and Liangzhen Lin for their help and useful discussions. This work was partially supported by the Beijing Municipal Science and Technology Commission under grant no. Z09010300820907, National ‘973’ Program (grant no. 2011CBA00105) and the National Natural Science Foundation of China (grant numbers 51025726 and 51002150).

New Journal of Physics 14 (2012) 033011 (http://www.njp.org/)
References

[1] Kamihara Y, Watanabe T, Hirano M and Hosono H 2008 J. Am. Chem. Soc. 130 3296
[2] Chen X H, Wu T, Wu G, Liu R H, Chen H and Fang D F 2008 Nature 453 376
[3] Chen G F, Li Z, Wu D, Li G, Hu W Z, Dong J, Zheng P, Luo J L and Wang N L 2008 Phys. Rev. Lett. 100 247002
[4] Wen H H, Mu G, Fang L, Yang H and Zhu X 2008 Europhys. Lett. 82 17009
[5] Ren Z A et al 2008 Chin. Phys. Lett. 25 2215
[6] Qi Y P, Gao Z S, Wang L, Wang D L, Zhang X P and Ma Y W 2008 Supercond. Sci. Technol. 21 115016
[7] Rotter M, Tegel M and Johrendt D 2008 Phys. Rev. Lett. 101 107006
[8] Sasmal K, Lv B, Lorenz B, Guloy A, Chen F, Xue Y and Chu C W 2008 Phys. Rev. Lett. 101 107007
[9] Wu G, Chen H, Wu T, Xie Y L, Yan Y J, Liu R H, Wang X F, Ying J J and Chen X H 2008 J. Phys.: Condens. Matter 20 422201
[10] Jeevan H S, Hossain Z, Kasinathan D, Rosner H, Geibel C and Gegenwart P 2008 Phys. Rev. B 78 092406
[11] Terashita T, Kimata M, Satsukawa H, Harada A, Hazama K, Uji S, Suzuki H, Matsumoto T and Murata K 2009 J. Phys. Soc. Japan 78 083701
[12] Wang X C, Liu Q Q, Lv Y X, Gao W B, Yang L X, Yu R C, Li F Y and Jin C Q 2008 Solid State Commun. 148 538
[13] Tapp J H, Tang Z J, Lv B, Sasmal K, Lorenz B, Chu P C W and Guloy A M 2008 Phys. Rev. B 78 060505(R)
[14] Parker D R, Pitcher M J, Baker P J, Franke I, Lancaster T, Blundell S J and Clarke S J 2009 Chem. Commun. 2189
[15] Hsu F C et al 2008 Proc. Natl Acad. Sci. USA 105 14262
[16] Marchand R and Jeitschko W 1978 J. Solid State Chem. 24 351
[17] Raffius H, Morsen E, Mosel B D, Muller-Warmuth W, Jeitschko W, Terbuchte L and Vombof T 1993 J. Phys. Chem. Solids 54 135
[18] Ren Z, Zhu Z W, Jiang S, Xu X F, Tao Q, Wang C, Feng C M, Cao G H and Xu Z A 2008 Phys. Rev. B 78 052501
[19] Jeevan H S, Hossain Z, Kasinathan D, Rosner H, Geibel C and Gegenwart P 2008 Phys. Rev. B 78 052502
[20] Ren Z, Tao Q, Jiang S, Feng C M, Wang C, Dai J H, Cao G H and Xu Z A 2008 Phys. Rev. Lett. 102 137002
[21] Qi Y P, Gao Z S, Wang L, Wang D L, Zhang X P and Ma Y W 2008 New J. Phys. 10 123003
[22] Chen G F, Li Z, Dong J, Li G, Hu W Z, Zhang X D, Song X D, Zheng P, Wang N L and Luo J L 2008 Phys. Rev. B 78 224512
[23] Wang X F, Wu T, Wu G, Chen H, Xie Y L, Ying J J, Yan Y J, Liu R H and Chen X H 2009 Phys. Rev. Lett. 102 117005
[24] Qi Y P, Gao Z S, Wang L, Zhang X P, Wang D L, Yao C, Wang C L, Wang C D and Ma Y W 2011 Europhys. Lett. 96 47005
[25] Werthamer N R, Helfand E and Hohenberg P C 1966 Phys. Rev. 147 295
[26] Dong C 1999 J. Appl. Cryst. 32 838
[27] Wang Z S, Luo H Q, Ren C and Wen H H 2008 Phys. Rev. B 78 140501(R)
[28] Jia Y, Cheng P, Fang L, Luo H Q, Yang H, Ren C, Shan L, Gu C Z and Wen H H 2008 Appl. Phys. Lett. 93 032503
[29] Guo J, Jin S, Wang G, Wang S, Zhu K, Zhou T, He M and Chen X 2010 Phys. Rev. B 82 180520(R)
[30] Mizuguchi Y, Takeya H, Kawasaki Y, Ozaki T, Tsuda S, Yamaguchi T and Takano Y 2011 Appl. Phys. Lett. 98 042511

New Journal of Physics 14 (2012) 033011 (http://www.njp.org/)