Superconductivity at 34.7 K in the iron arsenide \( \text{Eu}_{0.7}\text{Na}_{0.3}\text{Fe}_2\text{As}_2 \)

Yanpeng Qi, Zhaoshun Gao, Lei Wang, Dongliang Wang, Xianping Zhang and Yanwei Ma

Key Laboratory of Applied Superconductivity, Institute of Electrical Engineering, Chinese Academy of Sciences, P O Box 2703, Beijing 100190, People’s Republic of China

E-mail: ywma@mail.iee.ac.cn

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Abstract. \( \text{EuFe}_2\text{As}_2 \) is a member of the ternary iron arsenide family. Similar to \( \text{BaFe}_2\text{As}_2 \) and \( \text{SrFe}_2\text{As}_2 \), \( \text{EuFe}_2\text{As}_2 \) exhibits a clear anomaly in resistivity near 200 K. Here, we report the discovery of superconductivity in \( \text{Eu}_{0.7}\text{Na}_{0.3}\text{Fe}_2\text{As}_2 \) by partial substitution of the europium site with sodium. \( \text{ThCr}_2\text{Si}_2 \) tetragonal structure, as expected for \( \text{EuFe}_2\text{As}_2 \), is formed as the main phase for the composition \( \text{Eu}_{0.7}\text{Na}_{0.3}\text{Fe}_2\text{As}_2 \). Resistivity measurements reveal that the transition temperature \( T_c \) as high as 34.7 K is observed in this compound. The rate of \( T_c \) suppression with the applied magnetic field is 3.87 T K\(^{-1}\), giving an extrapolated zero-temperature upper critical field of 100 T. It demonstrates a very encouraging application of the new superconductors.

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1 Author to whom any correspondence should be addressed.
Realization of high-temperature superconductivity, even room-temperature superconductivity, is one of the ultimate goals in the field of materials science. The ongoing search for new superconductors has recently yielded a new family of Fe-based compounds LaFeAsO$_{1-x}$F$_x$ with transition temperatures $T_c$ up to 26 K [1]. By replacing La with other rare earths, $T_c$ can be raised to above 50 K [2]–[9], and thus the first non-copper-oxide superconductor with $T_c$ exceeding 50 K has emerged. Similar to the cuprates, the Fe–As layer is thought to be responsible for superconductivity and the R–O layer is a carrier reservoir layer to provide electron carriers. These discoveries have generated much interest in exploring even higher temperature superconductors, to open a new chapter in studies of high-temperature superconductivity outside the well-known domain of copper oxides.

Recently, the iron arsenide BaFe$_2$As$_2$ in a tetragonal ThCr$_2$Si$_2$-type structure has been found to show superconductivity at 38 K by hole doping with partial substitution of potassium for barium [10]. The BaFe$_2$As$_2$ compound is built up with identical Fe–As layers separated by Ba instead of R–O layers [11], so there are double Fe–As layers in the unit cell. Thereafter, SrFe$_2$As$_2$ and CaFe$_2$As$_2$ were synthesized successfully and superconductivity at 38 K was discovered by replacing the alkaline earth element with alkali elements [12]–[15]. EuFe$_2$As$_2$ is another member of the ternary iron arsenide family [16, 17]. The Eu in EuFe$_2$As$_2$ is divalent and similar to alkaline earth elements in chemical properties. EuFe$_2$As$_2$ exhibits a clear anomaly in resistivity near 200 K [18], which is similar to BaFe$_2$As$_2$ and SrFe$_2$As$_2$. This suggests that EuFe$_2$As$_2$ is another promising parent compound in which superconductivity may be realized by appropriate doping. Very recently, Jeevan et al reported high-temperature superconductivity in Eu$_{0.5}$K$_{0.5}$Fe$_2$As$_2$, in which K-doping suppresses the spin-density wave (SDW) transition and in turn gives rise to superconductivity at 32 K [19]. Sodium is similar to potassium in chemical properties and the Na$^+$ radius is close to Eu$^{2+}$. In this paper, we report the successful fabrication of Eu$_{0.7}$Na$_{0.3}$Fe$_2$As$_2$ by hole doping with partial substitution of sodium for europium. Similar to K-doping, Na-doping strongly weakens the anomaly and induces superconductivity at 34.7 K, which is comparable to the $T_c$ of Eu$_{0.5}$K$_{0.5}$Fe$_2$As$_2$ [19]. The upper critical fields ($H_{c2}$) determined according to the Werthamer–Helfand–Hohenberg formula are ($T = 0$ K) $\approx 100$ T, indicating a very encouraging application of the new superconductors.

1. Experimental

The superconductors with nominal composition of Na-doped Eu$_{0.7}$Na$_{0.3}$Fe$_2$As$_2$ were prepared by one-step solid state reaction. The details of fabrication process are described elsewhere [9]. Stoichiometric amounts of the starting elements Eu (99.99%), Na (99.5%), Fe (99.99%) and As (99.999%) were thoroughly ground by hand and encased into pure Nb tubes (one end of the tube was sealed). After packing, the other tube end was crumpled, and this tube was subsequently rotary swaged and sealed in an Fe tube. The sealed samples were slowly heated to 850 °C and kept at this temperature for 35 h. High purity argon gas was allowed to flow into the furnace during the heat-treatment process. It is noted that the sample preparation process except for annealing was performed in a glove box filled with a high purity argon atmosphere.

Phase identification and crystal structure investigation were carried out using x-ray diffraction (XRD) using Cu K$_\alpha$ radiation. Resistivity measurements were performed by the conventional four-point-probe method using a Quantum Design (PPMS). Ac magnetic susceptibility of the samples was measured with an Oxford cryogenic system (Maglab-12).
2. Results and discussion

The XRD pattern for the prepared sample is shown in figure 1. It is seen that all main peaks can be indexed by the ThCr\textsubscript{2}Si\textsubscript{2} tetragonal structure with \(a = 3.8978\)\ Å and \(c = 12.2623\)\ Å. It is noted that the lattice parameter values are \(a = 3.9104\)\ Å and \(c = 12.1362\)\ Å for the undoped compound EuFe\textsubscript{2}As\textsubscript{2} \[18\]. Clearly Na-doping leads to an apparent decrease in the \(a\)-axis lattice and an increase in the \(c\)-axis lattice. This result is similar to Ba\textsubscript{1-x}K\textsubscript{x}Fe\textsubscript{2}As\textsubscript{2} \[20\]. A small amount of FeAs impurity was also observed in the XRD pattern. Such impurity phases might be reduced by optimizing the heating process and stoichiometry ratio of the starting materials.

Figure 2 shows the temperature dependence of the electrical resistivity for Eu\textsubscript{0.7}Na\textsubscript{0.3}Fe\textsubscript{2}As\textsubscript{2}. From this figure, we can observe a sharp transition with the onset temperature at 34.7 K. The residual resistivity ratio (RRR) = \(\rho(300\) K)/\(\rho(35\) K) = 4.87, indicating the good quality of our sample. As reported by Ren et al undoped EuFe\textsubscript{2}As\textsubscript{2} exhibits a clear anomaly near 200 K \[18\], which is ascribed to the SDW instability and structural phase transitions from tetragonal to orthorhombic symmetry. Due to Na-doping, the high-temperature anomaly is suppressed and then superconductivity occurs. It is noted that a slight bump near 200 K is also seen in the resistivity curve. The anomaly is not completely suppressed, which suggests that \(T_c\) could be increased further as long as more sodium was doped into EuFe\textsubscript{2}As\textsubscript{2}.

In order to further confirm the superconductivity of Eu\textsubscript{0.7}Na\textsubscript{0.3}Fe\textsubscript{2}As\textsubscript{2}, ac magnetic susceptibility measurements were also performed. Figure 3 shows the temperature dependence of ac magnetization with a measuring frequency of 333 Hz and an amplitude of 0.1 Oe. The sample shows a well-diamagnetic signal and superconductivity with \(T_c = 32\) K, which corresponds to the middle transition point of resistance. The sharp magnetic transitions on ac curves indicate the good quality of our superconducting samples. Estimation on the magnetic signal indicates that the superconducting shielding volume of the sample is beyond 90%.

We carried out resistance versus temperature measurements for the Eu\textsubscript{0.7}Na\textsubscript{0.3}Fe\textsubscript{2}As\textsubscript{2} sample under different magnetic fields. The magnetic field is observed to suppress the transitions
as expected for a superconducting transition, the onset transition point and zero resistance point shift to lower temperatures. 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. Figure 4 shows the temperature dependence of $H_{c2}$ and $H_{irr}$ with magnetic fields up to 9 T for the Eu$_{0.7}$Na$_{0.3}$Fe$_2$As$_2$ sample. It is clear that the curve of $H_{c2}(T)$ is very steep with a slope of $-dH_{c2}/dT|_{T_c} = 3.87$ T K$^{-1}$. From this figure, using the Werthamer–Helfand–Hohenberg formula [21], $H_{c2}(0) = 0.693 \times (dH_{c2}/dT) \times T_c$. Taking $T_c = 33.7$ K, we can get $H_{c2}(0) \approx 90$ T. Adopting a criterion of 99% $\rho_n(T)$ instead of 90% $\rho_n(T)$, the $H_{c2}(0)$ value of this sample obtained by this equation is higher than 100 T. We can see that the irreversibility field is rather
Figure 4. The upper critical field $H_{c2}$ and $H_{irr}$ as a function of temperature for Eu$_{0.7}$Na$_{0.3}$Fe$_2$As$_2$ samples. The $H_{c2}$ and $H_{irr}$ values were defined as the 90 and 10% points of the resistive transition, respectively.

high compared to that in MgB$_2$. These high values of $H_{c2}$ and $H_{irr}$ indicate that this new superconductor has an encouraging application in very high fields. 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 $\sim 19$ Å ($H_{c2}(0) \approx 90$ T).

As we know, ThCr$_2$Si$_2$-type superconductor, $A$Fe$_2$As$_2$, is another member of the family of Fe–As superconductors. By replacing the alkaline earth elements with alkali elements, superconductivity was discovered in BaFe$_2$As$_2$, SrFe$_2$As$_2$ and CaFe$_2$As$_2$ [10]–[15], which caused excitement in the scientific community. The structure of $A$Fe$_2$As$_2$ superconductors is much simpler as compared to ZrCuSiAs-type compounds. More importantly, it is much easier to synthesize without oxygen and to grow large single crystals by the self-flux method, allowing the investigation of the intrinsic properties of the Fe–As superconductor. However, all $A$ elements come from alkaline earth elements. Very recently, Jeewan *et al* discovered high-temperature superconductivity in EuFe$_2$As$_2$ [18] and now, we report the superconductivity of Eu$_{0.7}$Na$_{0.3}$Fe$_2$As$_2$. It clearly demonstrates that EuFe$_2$As$_2$ is a new member of the ThCr$_2$Si$_2$-type Fe–As superconductor family [22], and offers the opportunity to study the mechanism of new iron-based superconductors.

3. Conclusions

To summarize, we have successfully synthesized the iron-based Na-doped layered compound Eu$_{0.7}$Na$_{0.3}$Fe$_2$As$_2$ by a one-step solid state reaction method. XRD diffraction shows that Eu$_{0.7}$Na$_{0.3}$Fe$_2$As$_2$ has ThCr$_2$Si$_2$ tetragonal structure with $a = 3.8978$ Å and $c = 12.2623$ Å. Na-doping leads to suppression of the anomaly partially in resistivity and induces superconductivity at 34.7 K. Furthermore, the upper critical fields ($H_{c2}$) determined according to the Werthamer–Helfand–Hohenberg formula are ($T = 0$ K) $\approx 100$ T, indicating a very encouraging application of the new superconductors.
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