Discovery of a novel 112-type iron pnictide and La-doping induced superconductivity in Eu$_{1-x}$La$_x$FeAs$_2$ (x = 0 ~ 0.15)

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Abstract:

We report the discovery and characterization of a novel 112-type iron pnictide EuFeAs$_2$, with La-doping induced superconductivity in a series of Eu$_{1-x}$La$_x$FeAs$_2$. The polycrystalline samples were synthesized through solid state reaction method only within a very narrow temperature window around 1073 K. Small single crystals were also grown from a flux method with the size about 100 µm. The crystal structure was identified by single crystal X-ray diffraction analysis as a monoclinic structure with space group of $P2_1/m$. From resistivity and magnetic susceptibility measurements, we found that the parent compound EuFeAs$_2$ shows a Fe$^{2+}$ related antiferromagnetic/structural phase transition near 110 K and a Eu$^{2+}$ related antiferromagnetic phase transition near 40 K. La doping suppressed the both phase transitions and induced superconducting transition with a $T_c \sim 11$ K for Eu$_{0.85}$La$_{0.15}$FeAs$_2$. 
1. Introduction

Since the first report of high-$T_c$ superconductivity in LaFeAs(O,F) at 26 K in 2008, hundreds of new layered iron pnictide superconductors have been discovered, with all of them formed by the typical Fe$_2$As$_2$ layers stacking with various types of blocking layers [1-10]. Among them, the 1111-type SmFeAs(O,F) still holds the highest $T_c$ around 55 K in bulk materials after 8 years [11]. Meanwhile, superconducting evidences around 100 K was reported in single unit cell film of FeSe on SrTiO$_3$ substrate [12]. Besides, some other layered transition metal pnictide superconductors were also discovered with much lower superconducting $T_c$ [13-15]. Therefore, it is still challenging to design and explore new iron-based superconductors with higher $T_c$ or novel structures for practical applications and physical research.

In all these iron pnictides, the newly reported 112-type Ca$_{1-x}$RE$_x$FeAs$_2$ (RE = La-Gd) superconductors are quite unique in crystal structure, which adopts a monoclinic space group with alternatively stacked Fe$_2$As$_2$ layers and Ca-As$_2$-Ca blocks, where the As$_2$ layers are made of unique zigzag As-As chains, with monovalent As$^-\,$ anions comparing with the trivalent As$^{3-}$ in Fe$_2$As$_2$ layer [9, 16-19]. Due to the special staggered intercalation layered crystal structure, recently CaFeAs$_2$ was also predicted to be an ideal candidate that integrates topological quantum spin Hall and superconductivity for the exploration of Majorana fermions [20, 21]. Unfortunately, the chemical phase of undoped CaFeAs$_2$ has never been obtained yet, and the only synthesized stable phases are the rare earth doped ones. The doping of rare earth metals introduce electrons and bring superconductivity in these 112-type compounds, while more doping of electrons may suppress the superconductivity and enhance the antiferromagnetism in the Fe$_2$As$_2$ layer unexpectedly [22, 23].

In this report, we have systematically studied the reacting conditions for the Eu-Fe-As ternary phases, and successfully synthesized the 112-type parent compound EuFeAs$_2$ for the first time. Through La-doping, superconductivity was induced in the Eu$_{1-x}$La$_x$FeAs$_2$ compounds with the $T_c$ up to 11 K.
2. Experimental details

The Polycrystalline samples for Eu$_{1-x}$La$_x$FeAs$_2$ ($x = 0, 0.05, 0.1, 0.15$) were synthesized by the solid state reaction method using EuAs, LaAs, and FeAs as precursors. The precursor materials were reacted by stoichiometric metal with Arsenic powder, which were mixed thoroughly and pressed into pellets, placed in alumina crucibles and sealed into Argon filled quartz tubes. The tubes were slowly heated to 1123 K and held for two days in a furnace. The powder of precursors were mixed in stoichiometric ratio of Eu$_{1-x}$La$_x$FeAs$_2$, and pressed into pellets. The pellets were placed in alumina crucibles and sealed into Argon filled quartz tubes. The tubes were slowly heated to 1073 K and held for one week. Single crystals of Eu$_{1-x}$La$_x$FeAs$_2$ were also attempted to grow by flux methods, and the grown crystals are with the size about 100 μm. All preparing manipulations were carried out in a glove box protected with high-purity argon gas.

Single crystal X-ray diffraction (SXRD) and powder X-ray diffraction (PXRD) were used for the identification of crystal structure and chemical phases. The sample resistivity was measured by the standard four-probe method using a Quantum Design physical property measurement system (PPMS), and the magnetic susceptibility was measured by a Quantum Design magnetic property measurement system (MPMS).

3. Results and discussions

The crystal structure for the Eu$_{1-x}$La$_x$FeAs$_2$ samples was determined by SXRD and PXRD analysis. Since the crystal growth is difficult, only one piece of well-shaped crystal with nominal composition of Eu$_{0.9}$La$_{0.1}$FeAs$_2$ was used for SXRD experiment, and the optical image of the crystal is shown in Fig. 1(a). The atomic composition for this crystal was analyzed by energy-dispersive X-ray spectroscopy (EDX) method, with the atomic ratio of Eu : La : Fe : As = 20.2 : 2.3 : 24.3 : 53.2. This result confirmed the 112-type composition, and the La-doping level is about 10.2%. Therefore, the nominal formula was used hereinafter. The crystallographic data
obtained from the SXRD analysis, the refined conditions, as well as the refined atomic coordinates and equivalent isotropic atomic displacement parameters were summarized in Table I. It confirms the chemical formula and reveals that the Eu$_{0.9}$La$_{0.1}$FeAs$_2$ crystal crystallizes in a monoclinic structure with space group $P2_1/m$ (No. 11), in accordance with the results of previously reported (Ca, Pr)FeAs$_2$ [16]. The crystal structure was depicted in Fig. 1(b).

All polycrystalline Eu$_{1-x}$La$_x$FeAs$_2$ samples were characterized by PXRD for structure analysis and phase identification. The PXRD patterns are presented in Fig. 1(c). Small amount of Eu$_2$O$_3$ and FeAs$_2$ impurities can be observed, and more impurities appear when the doping level $x$ increases. All the PXRD patterns were well indexed with the space group $P2_1/m$. The lattice parameters for the parent compound of EuFeAs$_2$ are refined to be $a = 3.980(0)$ Å, $b = 3.900(6)$ Å, $c = 10.643(9)$ Å, and $\beta = 90.035(1)$ °. For different La-doping levels, the lattice parameters have no obvious change due to the close radiuses of Eu$^{2+}$ and La$^{3+}$ ions. The La-doping levels were confirmed by EDX analysis, and we found the real La-doping levels are all close to the nominal ones in the polycrystalline samples.

The normalized resistivity data vs. temperature for all polycrystalline Eu$_{1-x}$La$_x$FeAs$_2$ samples were plotted in Fig. 2. All samples show metallic behavior below 300 K. For the undoped parent compound EuFeAs$_2$, two distinct anomalies appear around $T_N \sim 110$ K and $T_N \sim 40$ K respectively. The anomaly at 110 K is due to the Fe$^{2+}$ related antiferromagnetic/structural phase transition, as in other parent compounds of Fe-based superconductors [11, 24-28], as well as in Ca$_{1-x}$RE$_x$FeAs$_2$ [23, 29, 30]. The anomaly at 40 K indicates the antiferromagnetic (AFM) phase transition of Eu$^{2+}$ ions, as in EuFe$_2$As$_2$, EuCu$_2$As$_2$, EuPd$_2$Sb$_2$, etc. [27, 31, 32]. For the La-doping samples of Eu$_{1-x}$La$_x$FeAs$_2$, these two transitions are suppressed and shift to lower temperatures, but not completely eliminated even for $x = 0.15$. Meanwhile, a superconducting transition appears when $x = 0.05$, and the onset superconducting $T_c$ reaches 11 K when $x = 0.15$, which can be seen in the inset of Fig. 2. The coexistence of the superconducting phase with two AFM phases in the Eu$_{1-x}$La$_x$FeAs$_2$ system may
provide an ideal platform for the investigation of mutual interactions between the ordered electron states.

The temperature dependences of DC magnetic susceptibility were measured between 1.8 K and 300 K by the zero-field-cooling (ZFC) method for all polycrystalline Eu$_{1-x}$La$_x$FeAs$_2$ samples. The Eu$^{2+}$ related AFM transitions around $T_N \sim 40$ K for all samples are clearly revealed with similar transition temperatures indicated by the resistivity measurements, agreeing with the AFM behavior in other Eu-intercalated layered materials [27, 33, 34]. Doping La suppresses this AFM transition to lower temperature until $T_N \sim 27$ K when $x = 0.15$. The AFM transition around 110 K cannot be clearly observed due to the small magnetic moment of Fe$^{2+}$ comparing with Eu$^{2+}$. A weak superconducting transition appears for La-doping when $x = 0.05$, and it enhances when $x$ increases, with an onset $T_c$ about 8 K when $x = 0.15$. While all the polycrystalline Eu$_{1-x}$La$_x$FeAs$_2$ superconductors show very weak superconducting shielding volume fraction from the Meissner effect measurements.

To further confirm the La-doping induced superconductivity, the DC magnetic susceptibility for the above-mentioned single crystal Eu$_{0.9}$La$_{0.1}$FeAs$_2$ was also measured from 1.8 K to 10 K with both ZFC and FC methods under a 10 Oe magnetic field parallel to the c axis, as seen in Fig. 4. The Meissner effect shows typical type-II superconducting behavior. The onset superconducting $T_c$ is 6 K, and the estimated superconducting shielding volume fraction is 91% at 1.8 K. This indicates that La-doping actually induces bulk superconductivity in these novel Eu$_{1-x}$La$_x$FeAs$_2$ compounds.

In summary, a new 112-type iron pnictide EuFeAs$_2$ was discovered, with a monoclinic crystal structure by the space group of $P2_1/m$. The parent compound EuFeAs$_2$ shows two AFM phase transitions originating from the Fe$^{2+}$ layers and Eu$^{2+}$ layers. Upon La-doping, the AFM ordering was gradually suppressed and superconductivity simultaneously appears with a $T_c$ of 11 K in the polycrystalline Eu$_{0.85}$La$_{0.15}$FeAs$_2$. Bulk superconductivity was confirmed in the Eu$_{0.9}$La$_{0.1}$FeAs$_2$ single crystal from the Meissner effect measurements. Unlike the previously reported
meta-stable Ca-112 pnictides whose parent compound CaFeAs$_2$ cannot be obtained, these new Eu-112 pnictides provide a better system to study how the superconductivity evolves from the AFM ground state in the parent compound by electron-doping and possible emergent new physics inside this unique 112-type iron pnictide.

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Table I. Crystal structural parameters and atomic coordinates for Eu$_{0.9}$La$_{0.1}$FeAs$_2$ single crystal

| Chemical formula  | Eu$_{0.9}$La$_{0.1}$FeAs$_2$ |
|-------------------|-----------------------------|
| Crystal system    | Monoclinic                  |
| Space group       | $P2_1/m$ (No. 11)           |
| Lattice parameters|                             |
| $a$ (Å)           | 3.9820(17)                  |
| $b$ (Å)           | 3.8986(19)                  |
| $c$ (Å)           | 10.666(6)                   |
| $\alpha, \beta, \gamma$ (°) | 90, 90.240(18), 90 |
| $R1$              | 0.0455                      |
| Completeness      | 99.1%                       |
| Redundancy        | 3.11                        |
| $wR2$             | 0.1128                      |
| Independent reflections | 341                  |

| Atom  | $x/a$     | $y/b$ | $z/c$   | Occupancy | $U_{eq}$ (Å$^2$) |
|-------|-----------|-------|---------|-----------|-----------------|
| Eu    | 0.754(3)  | 0.75  | 0.7716(10) | 0.87(6)  | 0.0151(12)      |
| La    | 0.72(2)   | 0.75  | 0.760(6)  | 0.13(6)  | 0.025(15)       |
| As1   | 0.2504(5) | 0.25  | 0.6334(2) | 1         | 0.0167(8)       |
| As2   | 0.7502(6) | 0.25  | 0.9965(2) | 1         | 0.0252(8)       |
| Fe    | 0.2500(8) | 0.75  | 0.5000(3) | 1         | 0.0174(9)       |
Figure captions:

**Figure 1.** (a) The optical image for the Eu$_{0.9}$La$_{0.1}$FeAs$_2$ single crystal. (b) The crystal structure for the EuFeAs$_2$ compound. (c) Powder X-ray diffraction patterns for the Eu$_{1-x}$La$_x$FeAs$_2$ polycrystalline samples.

**Figure 2.** Temperature dependence of normalized resistivity for the Eu$_{1-x}$La$_x$FeAs$_2$ polycrystalline samples.

**Figure 3.** Temperature dependence of magnetic susceptibility for the Eu$_{1-x}$La$_x$FeAs$_2$ polycrystalline samples.

**Figure 4.** Temperature dependence of magnetic susceptibility for the Eu$_{0.9}$La$_{0.1}$FeAs$_2$ single crystal.
Fig. 1
Fig. 2
Fig. 3
Fig. 4

$\text{Eu}_{0.9}\text{La}_{0.1}\text{FeAs}_2$

$H \parallel c, 10 \text{ Oe}$