Superconductivity induced by oxygen deficiency in Sr-doped LaOFeAs

G. Wu, H. Chen, Y. L. Xie, Y. J. Yan, T. Wu, R. H. Liu, X. F. Wang, D. F. Fang, J. J. Ying and X. H. Chen

Hefei National Laboratory for Physical Science at Microscale and Department of Physics,
University of Science and Technology of China,
Hefei, Anhui 230026, P. R. China

(Dated: June 10, 2008)

We synthesized Sr-doped $La_{0.85}Sr_{0.15}OFeAs$ sample with single phase, and systematically studied the effect of oxygen deficiency in the Sr-doped LaOFeAs system. It is found that substitution of Sr for La indeed induces the hole carrier evidenced by positive thermoelectric power (TEP), but no bulk superconductivity is observed. The superconductivity can be realized by annealing the as-grown sample in vacuum to produce the oxygen deficiency. With increasing the oxygen deficiency, the superconducting transition temperature ($T_c$) increases and maximum $T_c$ reaches about 26 K the same as that in La(O,F)FeAs. TEP dramatically changes from positive to negative in the nonsuperconducting as-grown sample to the superconducting samples with oxygen deficiency. While $R_H$ is always negative for all samples (even for Sr-doped as grown sample). It suggests that the $La_{0.85}Sr_{0.15}O_{1-\delta}FeAs$ is still electron-type superconductor.

PACS numbers: 74.10. +v; 74.25. Fy; 74.25. Dw

Since the discovery of high-transition temperature ($T_c$) superconductivity in layered copper oxides, extensive efforts have been devoted to explore the higher $T_c$ superconductivity. Layered rare-earth metal oxypnictides LnOMPn ($Ln=$La, Pr, Ce, Sm; $M=$Fe, Co, Ni, Ru and $Pn=P$ and As) with ZrCuSiAs type structure[1, 2] have attracted great attention due to the discovery of superconductivity at $T_c = 26$ K in the iron-based $LaO_{1-x}F_xFeAs$ ($x=0.05-0.12$)[3]. $T_c$ was drastically raised to more than 40 K beyond McMillan limitation of 39 K predicted by BCS theory in $RO_{1-x}F_xFeAs$ by replacing La with other trivalent R with smaller ionic radii[4, 5, 6]. These discoveries have generated much interest for exploring novel high temperature superconductor, and provided a new material base for studying the origin of high temperature superconductivity.

Such high-$T_c$ iron pnictides adopts a layered structure of alternating Fe-As and Ln-O layers with eight atoms in a tetragonal unit cell. Similar to the cuprates, the Fe-As layer is thought to be responsible for superconductivity, and Ln-O layer is carrier reservoir layer to provide electron carrier. In order to induce the electron carrier, three different ways have been used: (1) substitution of fluorine for oxygen[3, 4]; (2) to produce oxygen deficiency[7]; and (3) substitution of $Th^{4+}$ for $Ln^{3+}$[8]. All these ways for inducing electron carrier are limited in the carrier reservoir Ln-O layer by substitution. The electron carrier induced transfers to Fe-As layer to realize superconductivity. Superconductivity at 25 K has been realized by hole doping with substituting $La^{3+}$ with $Sr^{2+}$ in LaOFeAs system[4]. The ternary iron arsenide $BaFe_2As_2$ shows superconductivity at 38 K by hole doping with partial substitution of potassium for barium[10]. The undoped material LaOFeAs shows an anomaly in resistivity at 150 K which is associated with the structural transition or SDW transition[9, 11]. The SDW and the anomaly in resistivity are suppressed, and superconductivity emerges with increasing F doping[10, 12]. No anomaly in resistivity is observed in optimal sample[10]. Therefore, the complete suppression of the anomaly peak is an indication for inducing carrier into system. Here we successfully prepared single phase $La_{0.85}Sr_{0.15}OFeAs$, and systematically studied the effect of oxygen deficiency on transport properties (resistivity, Hall coefficient, and thermoelectric power). It is found that substitution of $Sr^{2+}$ for $La^{3+}$ leads to the shift of the anomaly peak to high temperature. Thermoelectric power changes sign from negative to positive, while Hall coefficient keeps the same sign and its magnitude deceases with Sr doping. The superconductivity can be induced by annealing the as-grown sample in vacuum to produce the oxygen deficiency. Both TEP and $R_H$ is negative for the superconducting samples with oxygen deficiency. It suggests that the $La_{0.85}Sr_{0.15}O_{1-\delta}FeAs$ is still electron-type superconductor.

Polycrystalline samples with nominal composition LaOFeAs and $La_{0.85}Sr_{0.15}O_{1-\delta}FeAs$ were synthesized by conventional solid state reaction using high purity LaAs, SrCO$_3$, Fe, As and $Fe_2O_3$ as starting materials. LaAs was obtained by reacting La powder and As powder at 600 °C for 3 hours. The raw materials were thoroughly grounded and pressed into pellets. The pellets were wrapped into Ta foil and sealed in an evacuated quartz tube. They are then annealed at 1160 °C for 40 hours. The sample preparation process except for annealing was carried out in glove box in which high pure argon atmosphere is filled. The superconductivity is achieved with post-annealing of as-
LaOF_{x+y}eAs and La_{0.85}Sr_{0.15}O_{1-y}Fe_{x}As are shown in Fig. 2. The undoped compound LaOF_{x+y}eAs shows the same behavior as previous report[2] and an anomaly at 150 K, which is believed to be associated with the structural transition or SDW transition.\[11, 12\] As-grown Sr-doped LaOF_{x+y}eAs sample shows different temperature dependent behavior from that observed in the undoped LaOF_{x+y}eAs sample. The resistivity shows a linear temperature dependence above a characteristic temperature of \(\sim 165\) K, and steeply decreases with decreasing temperature below 165 K. Compared to the undoped LaOF_{x+y}eAs sample, the anomaly in resistivity shifts to high temperature of 165 K associated with the structural transition or SDW transition. The room-temperature resistivity is about 13.7 m\(\Omega\)cm, being larger than that of undoped LaOF_{x+y}eAs sample\((\sim 5\) m\(\Omega\)cm). However, a trace of superconducting transition at \(~ 6\) K is observed as shown in Fig. 2. The resistivity shows a weak temperature dependent behavior for the sample obtained by annealing the as-grown \(La_{0.85}Sr_{0.15}O_{1-y}Fe_{x}As\) sample in a high vacuum for 2 hours. The anomaly associated with the structural transition or SDW transition is still observed at \(~ 140\) K. Below 8 K, a superconducting behavior is observed, and no zero resistivity is obtained down to 4.2 K. The post-annealed \(La_{0.85}Sr_{0.15}O_{1-y}Fe_{x}As\) sample in high vacuum for 4 hours shows a well metallic behavior in resistivity and a sharp superconducting transition occurs at 26 K and reaches to zero at \(~ 23\) K. The resistivity behavior is very similar to that of

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**TABLE I: Lattice parameters for \(LaOF_{x+y}eAs\) and \(La_{0.85}Sr_{0.15}O_{1-y}Fe_{x}As\) samples with different annealing time**

| Annealing Time (hrs) | a (Å)       | c (Å)       |
|----------------------|-------------|-------------|
| Pure                 | 4.030(3)    | 8.730(5)    |
| 0 hrs                | 4.031(3)    | 8.749(5)    |
| 2 hrs                | 4.027(3)    | 8.730(5)    |
| 4 hrs                | 4.019(3)    | 8.723(5)    |

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FIG. 1: (color online) X-ray diffraction patterns at room temperature for the samples (a): \(LaOF_{x+y}eAs\); (b): as-grown \(La_{0.85}Sr_{0.15}O_{1-y}Fe_{x}As\); (c): post-annealed \(La_{0.85}Sr_{0.15}O_{1-y}Fe_{x}As\) in high vacuum for 2 hours; (d): post-annealed \(La_{0.85}Sr_{0.15}O_{1-y}Fe_{x}As\) in high vacuum for 4 hours.

FIG. 2: (color online) Temperature dependence of resistivity for the samples LaOF_{x+y}eAs (squares); as-grown \(La_{0.85}Sr_{0.15}O_{1-y}Fe_{x}As\) (circles); post-annealed \(La_{0.85}Sr_{0.15}O_{1-y}Fe_{x}As\) in high vacuum for 2 hours (triangles); post-annealed \(La_{0.85}Sr_{0.15}O_{1-y}Fe_{x}As\) in high vacuum for 4 hours (diamonds). The inset shows temperature dependent susceptibility for \(La_{0.85}Sr_{0.15}O_{1-y}Fe_{x}As\) annealed in high vacuum for 4 hours.
LaO$_{0.85}$F$_{0.11}$FeAs$^{[2]}$. The inset of Fig.2 shows the temperature dependent susceptibility in zero field cooling (ZFC) and field cooling (FC) for La$_{0.85}$Sr$_{0.15}$O$_{1-\delta}$FeAs annealed in high vacuum for 4 hours. Since the sample density is considerably smaller than the theoretical value, we use 100.7 cm$^3$/mol and get a superconducting fraction of $\approx 54\%$ shielding. It indicates a bulk superconductivity for La$_{0.85}$Sr$_{0.15}$O$_{1-\delta}$FeAs annealed in high vacuum for 4 hours.

The bulk superconductivity was realized by inducing oxygen deficiency, the electron-doping is expected by introduction of oxygen deficiency in Sr-doped LaOFeAs. In order to confirm this expectation and provide the direct evidence, the thermoelectric power and Hall coefficient are systematically measured. Temperature dependent Hall coefficients for all samples are shown in Fig.3. The sign of Hall coefficient for all samples are negative, indicating electron-type carrier in these samples. $R_H$ shows a sharp increase at the temperature of $\sim 150$ K associated with structure transition or SDW transition for the undoped LaOFeAs. Which is consistent with previous report$^{[12]}$. $R_H$ of the sample Sr-doped LaOFeAs shows similar temperature dependence to that of pure LaOFeAs. But Sr-doping leads to an decrease in magnitude of $R_H$, and seems to induce carrier into system. Fig.3 clearly shows that the sharp increase in $R_H$ occurs at $\sim 165$ K which coincides with the anomaly in resistivity shown in Fig.2. This further indicates that the sharp increase in $R_H$ arises from the SDW transition or structural phase transition. Annealing in vacuum leads to a decrease in $R_H$, and shift of the temperature corresponding to the sharp increase in $R_H$ to low temperature. It indicates that the annealing in high vacuum induces hole carrier and suppresses the SDW ordering, similar to effect of F-doping in SmO$_{1-\delta}$F$_x$FeAs$^{[14]}$. The superconducting sample obtained by annealing in high vacuum for 4 hours shows a very small $R_H$, and no sharp change in $R_H$ is observed above superconducting transition. It indicates complete supression of SDW transition or structural transition due to introduction of more electron-carrier into system.

Figure 4 shows the temperature dependence of thermoelectric power for all four samples. The parent compound LaOFeAs shows similar temperature dependent TEP to previous report$^{[12]}$, below the temperature ($\sim 150$ K) associated with SDW transition or structural transition, a broad peak shows up. Sr-doping in LaOFeAs leads to change the sign of TEP from negative to positive with decreasing temperature at 250 K. Its temperature dependence shows a typical behavior of a low carrier concentration materials which contains electrons and holes as discussed in Ref.12. Positive TEP indicates that the dominant carriers are holes, whereas $R_H$ has shown that electrons dominate. In particular, $R_H$ is always negative in entire temperature range. These experimental results are consistent with those of the band structure calculations which predicted that LaOFeAs is a multi-band system. The opposite signs of TEP ($>0$) and $R_H$ ($<0$) can be understood by considering that the methods of averaging contributions of multi-bands are different for TEP and $R_H$. It is striking that the annealing in high vacuum leads to change of TEP sign from positive to negative in entire temperature range. The temper-
ature dependence of TEP for the samples obtained by annealing in vacuum is similar to that of superconducting LaO$_{1-x}$Fe$_x$As\[15\]. At superconducting transition temperature, TEP sharply drops to zero. It is intriguing that the profile for temperature dependent TEP is similar to that of low carrier concentration metals like undoped high-$T_c$ cuprates except for negative sign. These results indicate that the dominate carriers are electron in superconducting Sr-doped LaOFeAs.

It should be pointed that no superconductivity can be realized in pure LaO$_{1-x}$Fe$_x$As by annealing in high vacuum, this is different from the report by Ren et al.\[7\]. Ren et al. reported that superconductivity can be obtained by high pressure preparation in LnO$_{1-\delta}$FeAs. High pressure preparation could produce enough oxygen deficiency, consequently induce the more carrier concentration to realize the superconductivity. While the annealing in vacuum cannot produce enough oxygen deficiency to obtain superconductivity. Much more oxygen deficiency could lead to the sample metastable. Such metastable sample can be obtained under high pressure, while it cannot reach under high vacuum. It could be reason why the superconductivity in LnO$_{1-\delta}$FeAs can only be obtain under pressure preparation. Sr-doping could play an important role in removing oxygen from lattice to produce more oxygen deficiency. This could reason why the superconductivity can be realized in Sr-doped La$_{0.85}$Sr$_{0.15}$O$_{1-\delta}$FeAs sample. Both TEP and $R_H$ definitely indicate that the dominant carrier is electron in superconducting La$_{0.85}$Sr$_{0.15}$O$_{1-\delta}$FeAs system. So far, it seems that n-type carrier can be induced into the system LnOFeAs with single FeAs layer, while p-type carrier is induced to the superconductors Ba$_{1-x}$K$_x$Fe$_2$As$_2$ with double FeAs layers\[16\]. It is different from the case of high-$T_c$ cuprates, it should be interesting issue.

Acknowledgment: This work is supported by the Nature Science Foundation of China and by the Ministry of Science and Technology of China (973 project No: 2006CB601001) and by National Basic Research Program of China (2006CB922005).

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