PHYSICAL REVIEW B **78**, 092503 (2008)

Superconductivity induced by oxygen deficiency in $La_{0.85}Sr_{0.15}FeAsO_{1-\delta}$

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(Received 10 June 2008; revised manuscript received 13 July 2008; published 16 September 2008)

We synthesized single phase $La_{0.85}Sr_{0.15}FeAsO_{1-\delta}$ samples and systematically studied the effect of oxygen deficiency in this system. It is found that partial substitution of Sr for La 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 oxygen deficiency, the superconducting transition temperature (T_c) increases and the maximum T_c reaches 26 K—the same as that observed in the $LaFeAsO_{1-x}F_x$ system. TEP changes the sign from positive for the nonsuperconducting as-grown sample to negative for the superconducting samples with oxygen deficiency, while R_H keeps negative for all samples. It suggests that the dominated carrier in $La_{0.85}Sr_{0.15}FeAsO_{1-\delta}$ is electronlike.

DOI: 10.1103/PhysRevB.78.092503 PACS number(s): 74.10.+v, 74.25.Dw, 74.25.Fy

Since the discovery of high-transition temperature (T_c) superconductivity in layered copper oxides, extensive efforts have been devoted to exploring 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 higher than 40 K beyond McMillan limitation of 39 K predicted by BCS theory in $LnO_{1-x}F_xFeAs$ by replacing La with other rare-earth Ln with smaller ionic radii.[4–6] These discoveries have generated much interest in exploring high-temperature superconductors and provided a kind of material base for studying the origin of high-temperature superconductivity.

Such high-T_c iron pnictides adopt 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 the Ln-O layer is the carrier reservoir layer that provides the electron carrier. In order to induce the electron carrier, three different ways have been used: (i) partial substitution of flourine for oxygen;[3,4] (ii) to produce oxygen deficiency;[7] and (iii) partial substitution of Th^{4+} for Ln^{3+}.[8] All these ways of inducing electron carriers into the system are limited to the substitution performed in the carrier reservoir Ln-O layer. The electron carrier induced transfers to the Fe-As layer to realize superconductivity. Superconductivity at 25 K realized by hole doping with substituting La^{3+} with Sr^{2+} in LaOFeAs system was reported.[9] The ternary iron arsenide $BaFe_2As_2$ shows superconductivity at 38 K with partial substitution of potassium for barium.[10] It is confirmed that the dominated carrier is holelike by Hall coefficient and thermoelectric power (TEP) measurements[11] in $Ba_{1-x}K_xFe_2As_2$.

The undoped material LaOFeAs shows an anomaly in resistivity at ~150 K, which is associated with the structural transition.[12] The structural transition and the anomaly in resistivity are suppressed and superconductivity emerges with increasing F doping.[13,14] No anomaly in resistivity is observed in the optimally doped sample.[14] Therefore, the complete suppression of the anomaly peak is an indication for inducing the carrier into the system. Here we successfully prepared single phase $La_{0.85}Sr_{0.15}FeAsO_{1-\delta}$ and systematically studied the effect of oxygen deficiency on transport properties (resistivity, Hall coefficient, and TEP). It is found that partial substitution of Sr^{2+} for La^{3+} leads to a shift of the anomaly peak in resistivity to high temperature and to a change of sign in TEP from negative to positive, while the 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 are negative for the superconducting samples with oxygen deficiency. It suggests that the dominated carrier in $La_{0.85}Sr_{0.15}O_{1-\delta}FeAs$ is electronlike.

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 with As powder at 600 °C for 3 h. 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 h. The sample preparation process (except for annealing) was carried out in a glove box in which high pure argon atmosphere is filled. The superconductivity is achieved with postannealing the as-grown samples $La_{0.85}Sr_{0.15}O_{1-\delta}FeAs$ for 2 and 4 h in a high-evacuated quartz, respectively. Figure 1 shows the x-ray diffraction (XRD) patterns for the polycrystalline samples LaOFeAs and $La_{0.85}Sr_{0.15}O_{1-\delta}FeAs$ obtained with different annealing times. All peaks in XRD patterns can be well indexed to the tetragonal ZrCuSiAs-type structure. The XRD patterns indicate that all samples are single phase and stable for annealing in vacuum. The XRD patterns just show subtle differences for all samples but the (122) and (114) peaks for the samples annealed in vacuum apparently shift to high angle. Table I shows lattice parameters for the sample LaOFeAs and variation of lattice parameters with annealing time for the samples $La_{0.85}Sr_{0.15}O_{1-\delta}FeAs$ with different oxygen vacancy. It shows that both a-axis and c-axis lattice parameters decrease systematically with annealing time. Increase in the annealing

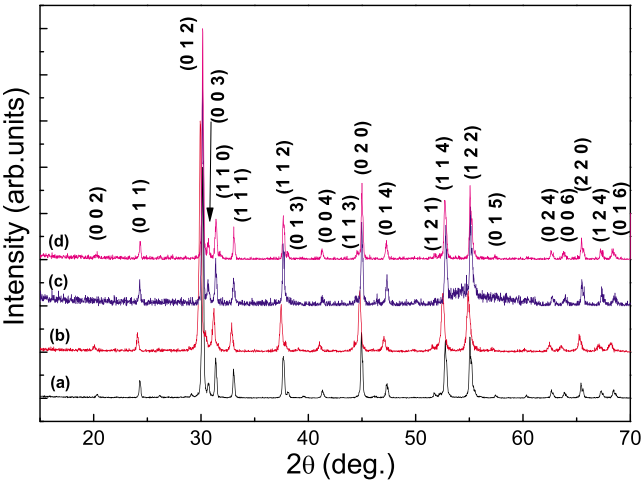

FIG. 1. (Color online) X-ray diffraction patterns at room temperature for the samples: (a) LaOFeAs; (b) as-grown $La_{0.85}Sr_{0.15}O_{1-\delta}FeAs$; (c) postannealed $La_{0.85}Sr_{0.15}O_{1-\delta}FeAs$ in high vacuum for 2 h; and (d) postannealed $La_{0.85}Sr_{0.15}O_{1-\delta}FeAs$ in high vacuum for 4 h.

time in high vacuum leads to more oxygen deficiency. It suggests that the lattice parameters a and c decrease with increasing oxygen deficiency. Such variation of lattice parameters with oxygen deficiency is consistent with a previous report in $NdO_{1-\delta}FeAs$.[7]

Temperature-dependent resistivity for the samples LaOFeAs and $La_{0.85}Sr_{0.15}O_{1-\delta}FeAs$ is shown in Fig. 2. The undoped compound LaOFeAs shows the same resistivity behavior as the previous report.[3] The anomaly at 150 K in resistivity is believed to be associated with the structural transition.[12] As-grown Sr-doped LaOFeAs sample shows different temperature-dependent behavior from that observed in the undoped LaOFeAs sample. The resistivity shows a linear temperature dependence above a characteristic temperature of ~165 K and steeply decreases with decreasing temperature below 165 K. The anomaly in resistivity shifts to high temperature of 165 K associated with the structural transition or spin-density wave (SDW) transition relative to the undoped LaOFeAs sample. The room-temperature resistivity is about 13.7 mΩ cm, which is larger than that of the undoped LaOFeAs sample (~5 mΩ 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 $La_{0.85}Sr_{0.15}OFeAs$ sample in a high vacuum for 2 h. The anomaly associated with the structural transition or SDW transition is still observed at ~140 K. A superconducting transition at 8 K is observed and no zero resistivity is obtained with temperature down to 4.2 K. The postannealed $La_{0.85}Sr_{0.15}O_{1-\delta}FeAs$ sample in high vacuum for 4 h shows a well-metallic behavior. A sharp superconducting transition occurs at 26 K and the resistivity reaches to zero at ~23 K. Temperature dependence of resistivity is very similar to that of the superconducting $LaO_{0.89}F_{0.11}FeAs$.[3] The inset of Fig. 2 shows the temperature-dependent susceptibility in zero-field cooling and field cooling for $La_{0.85}Sr_{0.15}O_{1-\delta}FeAs$ annealed in high vacuum for 4 h. Since the sample density is considerably smaller than the theoretical value, we use 100.7 cm^3/mol to estimate the superconducting volume and get a superconducting fraction of ≈54% shielding. It definitely indicates a bulk superconductivity for $La_{0.85}Sr_{0.15}O_{1-\delta}FeAs$ annealed in high vacuum for 4 h.

TABLE I. Lattice parameters for the samples LaOFeAs and $La_{0.85}Sr_{0.15}O_{1-\delta}$ FeAs with different oxygen deficiency.

Sample	a (Å)	c (Å)
Pure	4.030(3)	8.736(5)
Annealing time	a (Å)	c (Å)
0 h	4.031(3)	8.749(5)
2 h	4.027(3)	8.730(5)
4 h	4.019(3)	8.723(5)

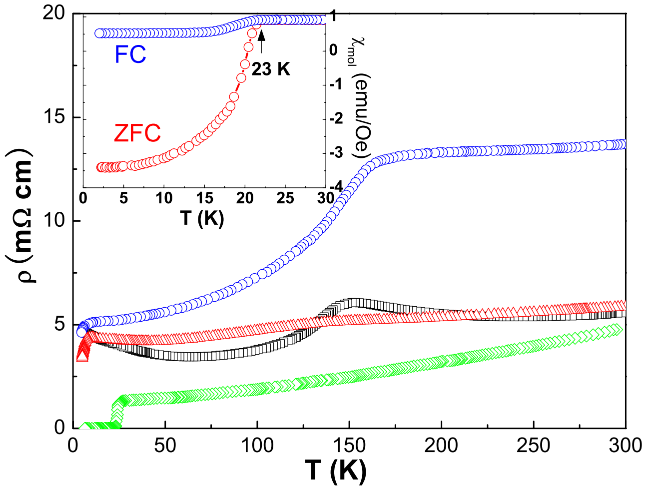

FIG. 2. (Color online) Temperature dependence of resistivity for the samples: LaOFeAs (squares); as-grown $La_{0.85}Sr_{0.15}O_{1-\delta}FeAs$ (circles); postannealed $La_{0.85}Sr_{0.15}O_{1-\delta}FeAs$ in high vacuum for 2 h (triangles); and postannealed $La_{0.85}Sr_{0.15}O_{1-\delta}FeAs$ in high vacuum for 4 h (diamonds). The inset shows temperature-dependent susceptibility for $La_{0.85}Sr_{0.15}O_{1-\delta}FeAs$ annealed in high vacuum for 4 h.

Since the bulk superconductivity was realized by inducing oxygen deficiency, the electron doping is expected by the introduction of oxygen deficiency in Sr-doped LaOFeAs. In order to confirm this expectation and provide the direct evidence, the TEP and Hall coefficient (R_H) are systematically measured. Temperature-dependent Hall coefficients for all samples are shown in Fig. 3. The sign of the Hall coefficient for all samples is negative, indicating that the dominated carrier is electronlike in these samples. The magnitude of R_H shows a sharp increase in the temperature of ~150 K associated with structure transition or SDW transition for the undoped LaOFeAs. Such behavior has been widely observed in parent compounds.[14]

R_H of the sample Sr-doped LaOFeAs shows similar temperature dependence to that of pure LaOFeAs. But Sr doping leads to a decrease in magnitude of R_H, suggesting that it seems to induce carriers into the system. Figure 3 clearly shows that the sharp increase in magnitude of R_H occurs at

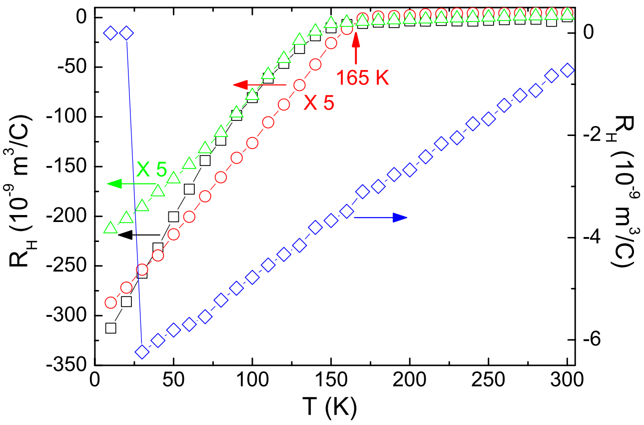

FIG. 3. (Color online) Temperature dependence of Hall coefficient for the samples: LaOFeAs (squares); as-grown $La_{0.85}Sr_{0.15}OFeAs$ (circles); postannealed $La_{0.85}Sr_{0.15}O_{1-\delta}FeAs$ in high vacuum for 2 h (triangles); and postannealed $La_{0.85}Sr_{0.15}O_{1-\delta}FeAs$ in high vacuum for 4 h (diamonds).

~165 K, which coincides with the anomaly of resistivity at 165 K shown in Fig. 2 for the Sr-doped sample. This further indicates that the sharp increase in magnitude of R_H arises from the SDW transition or structural phase transition. Annealing in vacuum leads to a decrease in magnitude of R_H and a shift of the temperature corresponding to the sharp increase in magnitude of R_H to low temperature. It indicates that the annealing in high vacuum induces electron carriers into the system and suppresses the structural transition or SDW ordering, which is similar to the effect of F doping in $SmO_{1-x}F_xFeAs$.[14] The superconducting sample obtained by annealing as-grown sample in high vacuum for 4 h shows a very small negative R_H, indicating the introduction of enough electron carriers into the system to realize superconductivity. No steep increase in magnitude of R_H is observed above superconducting transition temperature. It indicates complete suppression of SDW transition or structural transition due to introduction of more electron carriers into the system. A sharp decrease in magnitude of R_H to zero at 26 K happens due to the occurrence of superconductivity.

Figure 4 shows the temperature dependence of TEP for all four samples. The parent compound LaOFeAs shows negative TEP. With decreasing temperature, negative TEP increases and the negative TEP starts to decrease below ~150 K at which a structural transition is observed[12] and a broad peak around 125 K associated with SDW transition or structural transition shows up. Sr doping in (La,Sr)OFeAs system leads to a change in the sign of TEP from negative to positive at 250 K with decreasing temperature. Its temperature dependence shows a typical behavior of low carrier-concentration materials, which contain electrons and holes as discussed in Ref. 15. 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 the entire temperature range. These experimental results are consistent with those of the band-structure calculations, which predicted that LaOFeAs is a multiband system. The opposite signs of TEP (>0) and R_H (<0) can be understood by considering that averaging contributions of multibands are different for TEP and R_H.

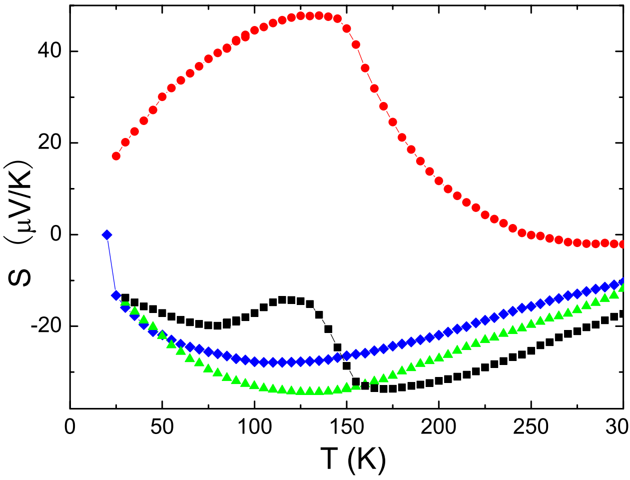

FIG. 4. (Color online) Temperature-dependent thermoelectric power for the samples: LaOFeAs (squares); as-grown $La_{0.85}Sr_{0.15}O_{1-\delta}FeAs$ (circles); postannealed $La_{0.85}Sr_{0.15}O_{1-\delta}FeAs$ in high vacuum for 2 h (triangles); and postannealed $La_{0.85}Sr_{0.15}O_{1-\delta}FeAs$ in high vacuum for 4 h (diamonds).

To understand the different signs between the Hall coefficient and TEP, the simplest model beyond the one-carrier free-electron approximation is a two-band model, considering the case of a current carried by both electrons (concentration n_e, mobility μ_e, and conductivity σ_e) and holes (n_p, μ_p, and σ_p). The Hall coefficient and TEP within a two-band model are given by[16,17]

$$R_H = \frac{n_p\mu_p^2 - n_e\mu_e^2}{e(n_p\mu_p^2 + n_e\mu_e^2)}, \tag{1}$$

where $e>0$ is the elementary charge.

$$S = (\sigma_e/\sigma)S_e + (\sigma_p/\sigma)S_p, \tag{2}$$

where $\sigma=\sigma_e+\sigma_p$.

Based on the above formula, it is easy to understand that Sr doping leads to a decrease in negative Hall coefficient and change of sign in TEP. Sr doping leads to an increase in hole concentration (n_p) so that R_H decreases. But the $n_p\mu_p^2$ is still less than $n_e\mu_e^2$ and the R_H keeps negative. Increase in hole concentration induced by Sr doping strongly enhances the hole conductivity σ_p and S_p so that the sign of S changes. Postannealing in high vacuum leads to the production of the oxygen deficiency, resulting in an increase in electron concentration (n_e) and enhancing the contribution from electron carrier to S. Therefore, postannealing in high vacuum leads to the decrease in R_H and change of TEP sign from positive to negative in the entire temperature range. The temperature dependence of TEP for the samples obtained by annealing in vacuum is similar to that of superconducting $LaO_{1-x}F_xFeAs$.[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 such as undoped high-T_c cuprates except for negative sign. These results indicate that the dominant carriers are electron in superconducting $La_{0.85}Sr_{0.15}O_{1-\delta}FeAs$.

It should be pointed that no superconductivity can be realized in pure $LaO_{1-\delta}FeAs$ by annealing in high vacuum, which 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 inducing 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 metastable sample. Such metastable sample can be obtained under high pressure, while it cannot be reached under high vacuum. It could be the reason why the superconductivity in $LnO_{1-\delta}FeAs$ can only be obtained under high-pressure preparation. Sr doping could play an important role in removing oxygen from the lattice to produce more oxygen deficiency. This could be the reason why the superconductivity can be realized in Sr-doped $La_{0.85}Sr_{0.15}O_{1-\delta}FeAs$ sample by annealing in vacuum. Both TEP and R_H definitely indicate that the dominant carrier is an electron in the 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 $Ba_{1-x}K_xFe_2As_2$ with double FeAs layers.[11] It is different from the case of high-T_c cuprates and it should be an interesting issue.

This work was supported by the Nature Science Foundation of China, by the Ministry of Science and Technology of China (973 Project No. 2006CB601001), and by the National Basic Research Program of China (Project No. 2006CB922005).

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