Transport and magnetic properties of La-doped $CaFe_2As_2$

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We measured the transport properties and susceptibility of single-crystal $Ca_{1-x}La_xFe_2As_2$ ($x = 0$, 0.05, 0.1, 0.15, 0.19, and 0.25). Large in-plane resistivity anisotropy similar to that in Co-doped 122 iron pnictides is observed although no transition metals were introduced in the FeAs plane. The in-plane resistivity anisotropy gradually increases with La doping below T_{SDW}, being different from the hole-doped 122 superconductors. The susceptibilities of the samples show that La doping leads to suppression of the spin-density wave (SDW) and induces a Curie-Weiss-like behavior at low temperature, which is much stronger than the other 122 iron-based superconductors.

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I. INTRODUCTION

Iron-based superconductors have attracted great attentions recently.[1–4] The parent compound undergoes structure and spin-density wave (SDW) transitions. With chemical doping or high pressure, both structure and SDW transition can be suppressed and superconductivity emerges. AFe_2As_2 ($A =$ Ca, Sr, Ba, Eu, so-called 122) with the $ThCr_2Si_2$-type structure were widely investigated because it is easy to grow a large size of high-quality single crystals. However, the highest T_C of 122 superconductors do not surpass 40 K in the earlier studies. Recently, superconductivity up to 49 K was discovered in rare-earth-doped $CaFe_2As_2$.[5–8] The FeAs plane of $Ca_{1-x}R_xFe_2As_2$ ($R =$ rare earth elements) is not affected by substitution of trivalent R^{3+} ions on divalent Ca^{2+}. While for the other two famous electron-doped 122 superconductors $BaFe_{2-x}Co_xAs_2$ and $K_xFe_{2-y}Se_2$, some of the Fe ions in the FeAs/FeSe layers are either substituted by Co or missed.[9–11] It is an ideal candidate for us to investigate the electron-doped iron-based superconductors with the perfect FeAs layers. The superconducting temperature in $Ca_{1-x}R_xFe_2As_2$ is much higher compared to the other 122 iron pnictides and it is very necessary for us to investigate in detail the physical properties of $Ca_{1-x}R_xFe_2As_2$.

Recent works showed large in-plane resistivity anisotropy below T_S or T_N in the parent and electron-doped 122 system although the distortion of the orthorhombic structure is less than 1%[12–15] in the SDW state. However, for the hole-doped $Ba_{1-x}K_xFe_2As_2$, in-plane resistivity anisotropy is nearly absent.[14] All the previous works focused on the Co, Ni, and Cu substitution on the Fe site for electron-doped samples[16] and it is supposed that the large in-plane anisotropy might come from the transition metal substitution in the FeAs plane. It is very meaningful for us to study the in-plane resistivity anisotropy for the electron-doped $Ca_{1-x}R_xFe_2As_2$ with the perfect Fe square lattice. The large in-plane anisotropy observed in $Ca_{1-x}R_xFe_2As_2$ in this paper indicates that the large in-plane resistivity anisotropy is related to the electron-doping rather than the transition metal doped in the FeAs plane.

In this paper, we systematically investigated the transport and magnetic properties of La-doped $CaFe_2As_2$. Superconductivity up to 43 K was observed in the $Ca_{0.81}La_{0.19}Fe_2As_2$ similar to the previous results.[6] SDW transition can be suppressed through La doping and superconductivity coexists with antiferromagnetism at the La doping level between 0.05 and 0.15. The in-plane resistivity anisotropy gradually increases with La doping below T_{SDW}, being different from the hole-doped 122 superconductors. A strong Curie-Weiss-like behavior at low temperature is induced by La doping.

II. EXPERIMENT

High-quality single crystals with nominal composition $Ca_{1-x}La_xFe_2As_2$ ($x = 0$, 0.05, 0.1, 0.15, 0.2, and 0.3) were grown by conventional solid-state reaction using FeAs as self-flux.[6–8] The FeAs precursor was first synthesized from stoichiometric amounts of Fe and As inside the silica tube at 800 °C for 24 h. Appropriate amounts of the starting materials of FeAs, Ca, and La were placed in an alumina crucible, and sealed in a quartz tube. The mixture was heated to 1180 °C in 6 hours and then kept at this temperature for 10 hours, and later slowly cooled down to 950 °C at a rate of 3 °C/hour. After that, the temperature was cooled down to room temperature by shutting down the furnace. The shining platelike $Ca_{1-x}La_xFe_2As_2$ crystals were mechanically cleaved from the flux and obtained for measurements. The actual composition of the single crystals was characterized by energy-dispersive x-ray spectroscopy (EDX). The actually doping levels are almost the same with the nominal values for x smaller than 0.2. While for the nominal composition $x = 0.2$ and 0.3, the actual values of x are 0.19 and 0.25, which are smaller than the nominal values. Resistivity was measured using the Quantum Design PPMS-9 and magnetic susceptibility was measured using the Quantum Design SQUID-MPMS. In-plane resistivity anisotropy was measured using the same method as the previous work.[12,14] Crystals were cut parallel to the orthorhombic a and b axes so that the orthorhombic a (b) direction is perpendicular (parallel) to the applied pressure direction. ρ_a (current parallel to a) and ρ_b (current parallel to b) were measured on the same sample using standard four-point configuration.

III. RESULTS AND DISCUSSION

Single crystals of $Ca_{1-x}La_xFe_2As_2$ were characterized by x-ray diffractions (XRD) using Cu K_α radiations. As shown

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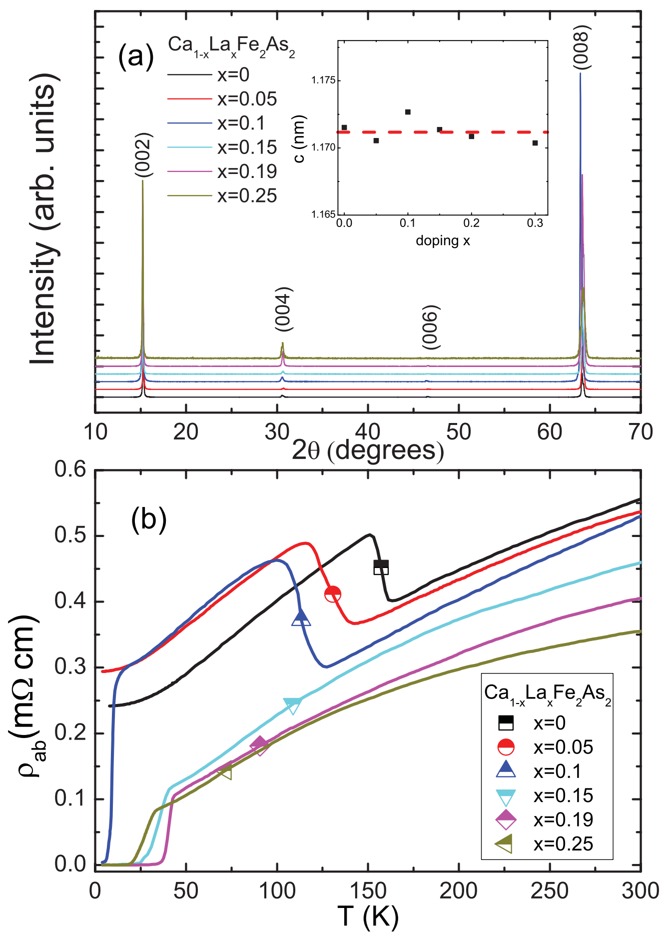

FIG. 1. (Color online) (a) The single-crystal x-ray diffraction pattern of $Ca_{1-x}La_xFe_2As_2$, Only (00*l*) diffraction peaks show up, indicating that the *c* axis is perpendicular to the plane of the plate. The inset shows that the *c* parameter does not changes with doping. (b) Temperature dependence of the in-plane resistivity.

in the Fig. 1(a), only (00*l*) diffraction peaks were observed, suggesting that the crystallographic *c* axis is perpendicular to the plane of the single crystal. The inset of Fig. 1(a) shows the *c*-axis parameters with different doping level. We can see that the lattice parameters of the *c* axis almost do not change with La doping. The lattice constant of the *c* axis was around 11.72 Å for all the samples. It is slightly different from the polycrystalline samples reported previously for which the *c* axis slightly decreases with rare earth elements doping.[5] Figure 1(b) shows the temperature dependence of the resistivity with the electric current flowing in the *a*-*b* plane for $Ca_{1-x}La_xFe_2As_2$ single crystals. The upturn of resistivity for parent compound was ascribed to the SDW or structure transition. With La doping, the anomaly was gradually suppressed and superconductivity gradually emerged. For the optimal-doped sample $x = 0.19$, the onset of superconductivity was up to 43 K, which is almost the same with the earlier results.[6] However, the superconductivity transition in this system is much broader than that in other 122 iron pnictide superconductors.

Figure 2(a) shows the temperature dependence of in-plane resistivity with the current flowing parallel to the orthorhombic *b* direction (black) and orthorhombic *a* direction (red) of the detwinned $CaFe_2As_2$ sample. Figures 2(e) and 2(f) are the polarized-light images of the surface for twinned and detwinned $CaFe_2As_2$ at the temperature of 78 K, respectively. The samples are almost fully detwinned as we can no longer see the twin domains. Obvious anisotropy was observed, which is similar to the earlier result,[13] although different methods were used to detwin the samples. Compounds with a small amount of La doping show much larger in-plane anisotropy as displayed in Figs. 2(b) and 2(c) for $x = 0.05$ and $x = 0.1$, respectively. The different behavior of ρ_a and ρ_b observed here is very similar to the one in other parent or electron-underdoped iron pnictides.[12,13] We characterized the degree of in-plane resistivity anisotropy by the ratio ρ_b/ρ_a. Figure 2(d) shows the temperature dependence of ρ_b/ρ_a for different doping level samples. For all the samples, in-plane resistivity anisotropy increases very quickly below T_{SDW}. With increasing La doping level, the in-plane resistivity anisotropy gradually increases in the SDW region. This is very similar with the other underdoped electron-doping 122 systems, but quite different from the hole-doped $Ba_{1-x}K_xFe_2As_2$.[14] Although the doping position is away from the FeAs plane, large in-plane anisotropy still exists and increases with doping content. The magnitude of in-plane resistivity anisotropy is almost the same as the other underdoped electron-doping 122 samples. These results suggest that the in-plane anisotropy is closely related to the carrier type rather than the different doping positions

The temperature dependence of magnetic susceptibilities for $Ca_{1-x}La_xFe_2As_2$ ($x = 0, 0.05,$ and 0.1) with magnetic field of $H = 1T$ applied along the *a*-*b* plane are shown in Fig. 3(a). The susceptibility of parent compound $CaFe_2As_2$ shows *T*-linear behavior and gradually decreases with decreasing temperature above T_{SDW}. The susceptibility suddenly drops at T_{SDW} and shows very weak Curie-Weiss-like behavior at low temperature. This behavior is the same as the previous result.[17] A small doping amount of La obviously enhances the Curie-Weiss-like behavior at low temperature. With an increase of the doping content, the anomaly due to SDW order is gradually suppressed and the *T*-linear behavior of susceptibility is gradually broken due to the Curie-Weiss-like behavior at low temperature. This strongly contrasts to Co-doped 122 samples in which the *T*-linear behavior of susceptibility survives with Co doping.[18] With a further increase of the doping content, the susceptibilities showed strong Curie-Weiss-like behavior below about 200 K as shown in Fig. 3(b). Such strong Curie-Weiss-like behavior observed in $Ca_{1-x}La_xFe_2As_2$ is strongly different to the other 122 iron pnictide superconductors.

Figure 4(a) shows the temperature dependence of Hall coefficient R_H of $Ca_{1-x}La_xFe_2As_2$. R_H of all the samples shows negative values, indicating that the dominated carrier is the electron. The sharp increase of the absolute value of R_H below T_{SDW} indicates the sudden drop of carrier density in the SDW state, which is the common feature in iron pnictide superconductors.[19] It is also instructive to analyze the Hall coefficient at certain temperatures for different doping level samples at high temperature. It is found that the dependence of doping is nonmonotonic as shown in Fig. 4(b). For the samples $x < 0.15$, the absolute value of R_H increases with increasing the doping content. With further doping, it gradually decreases.

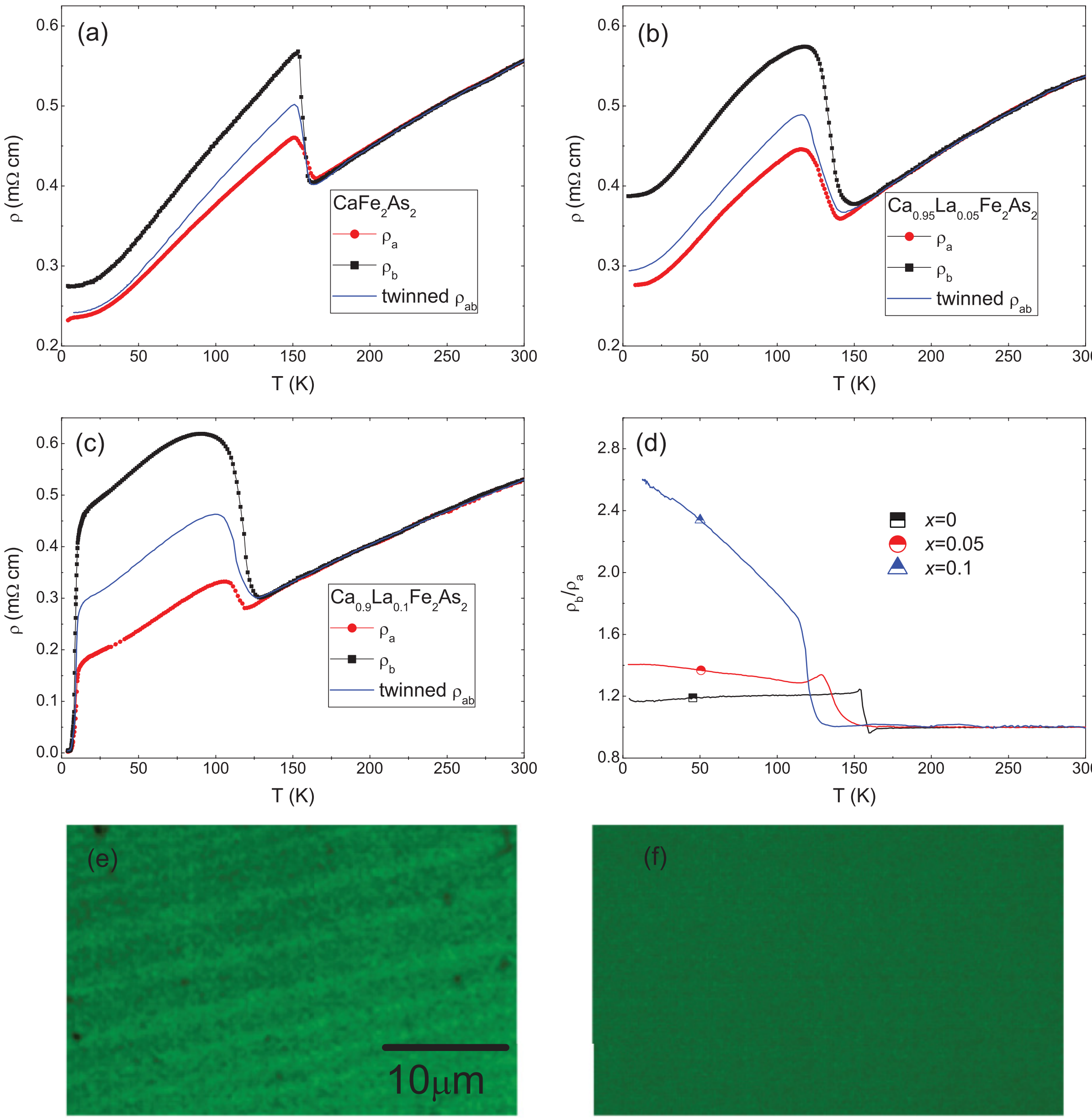

FIG. 2. (Color online) Temperature dependence of in-plane resistivity with the electric current flow along *a* direction and *b* direction respectively for (a) parent compound $CaFe_2As_2$, (b) $Ca_{0.95}La_{0.05}Fe_2As_2$, (c) $Ca_{0.9}La_{0.1}Fe_2As_2$. The twinned in-plane resistivity was also shown for comparison (blue line). (d) Temperature dependence of in-plane resistivity anisotropy ρ_b/ρ_a. (e) and (f) show the polarized-light images of the surface for twinned and detwinned $CaFe_2As_2$ at the temperature of 78 K, respectively.

This behavior is quite similar to the $BaFe_{2-x}Co_xAs_2$ system. Such behavior is caused by the multiband effect and different mobility of electron or hole carriers.[19]

Large in-plane anisotropy is observed in the underdoped region of $Ca_{1-x}La_xFe_2As_2$ although no extra elements were introduced into the FeAs plane. This strongly contrasts to the hole-doped $Ba_{1-x}K_xFe_2As_2$ system, but is similar to the transition metal substitution samples.[12,14] Our results show that substitution away from the FeAs plane could also lead to large in-plane anisotropy, which indicates that the in-plane anisotropy is strongly dependent on doping carriers rather than the doping site. The in-plane anisotropy was suggested closely related to the orbital degree of freedom[20,21] and/or spin fluctuations.[22] Our previous work demonstrates that the microscopic orbital involvement in the magnetically ordered state must be fundamentally different between the hole and electron underdoped iron pnictides.[14] Large in-plane anisotropy observed in rare earth doped materials also prove this. Angle-resolved photoelectron spectroscopy (ARPES) experiments are needed to compare the orbital characters of the hole and electron doped samples. The magnetic susceptibilities of $Ca_{1-x}La_xFe_2As_2$ show much stronger Curie-Weiss-like behavior compared to the other 122 iron pnictide superconductors. Although superconductivity above 40 K was observed in this system, which is much higher than the other 122 superconductors, superconducting transition is

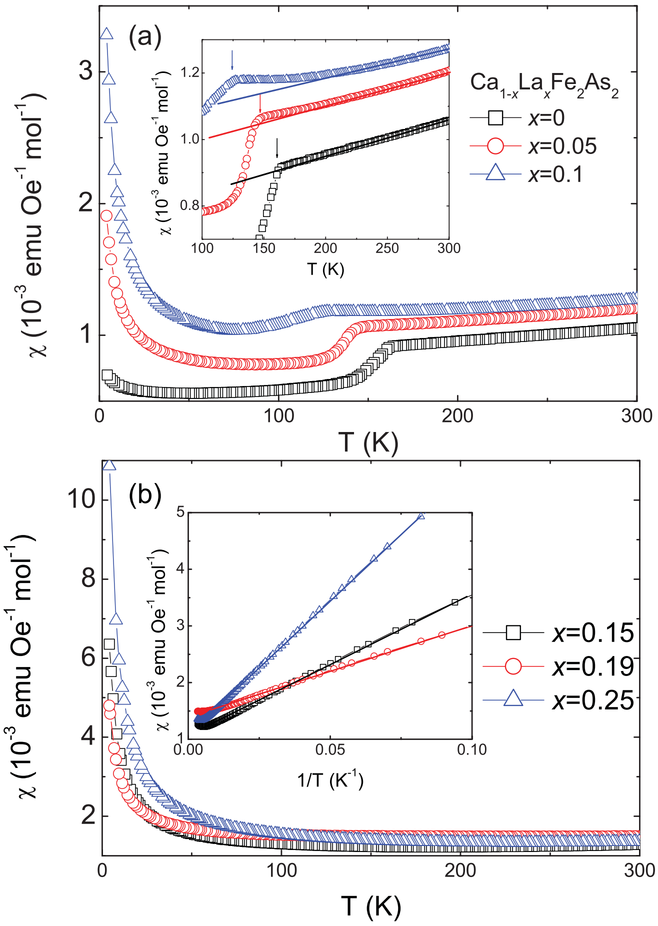

FIG. 3. (Color online) (a) Temperature dependence of magnetic susceptibility for $x = 0$, 0.05, and 0.1. The inset is the enlarged area around T_{SDW}. The arrows indicate the T_{SDW}. (b) Temperature dependence of magnetic susceptibility for $x = 0.15$, 0.19, and 0.25. The inset shows that the magnetic susceptibility is linear with $1/T$ at low temperature, indicating a nice Curiew-Weiss behavior at the low temperature.

broad. The origins of the strong Curie-Weiss-like behavior and broad superconducting transition in this system are still unknown.

IV. CONCLUSION

In conclusion, we systematically measured the transport properties and susceptibilities of $Ca_{1-x}La_xFe_2As_2 (x = 0$, 0.05, 0.1, 0.15, 0.19, and 0.25). Large in-plane anisotropy is observed, which is similar to Co-doped 122 ironpnictides, but strongly contrasts to the hole-doped $Ba_{1-x}K_xFe_2As_2$. Strong Curie-Weiss-like behavior of susceptibility was observed at low temperature by increasing the La doping.

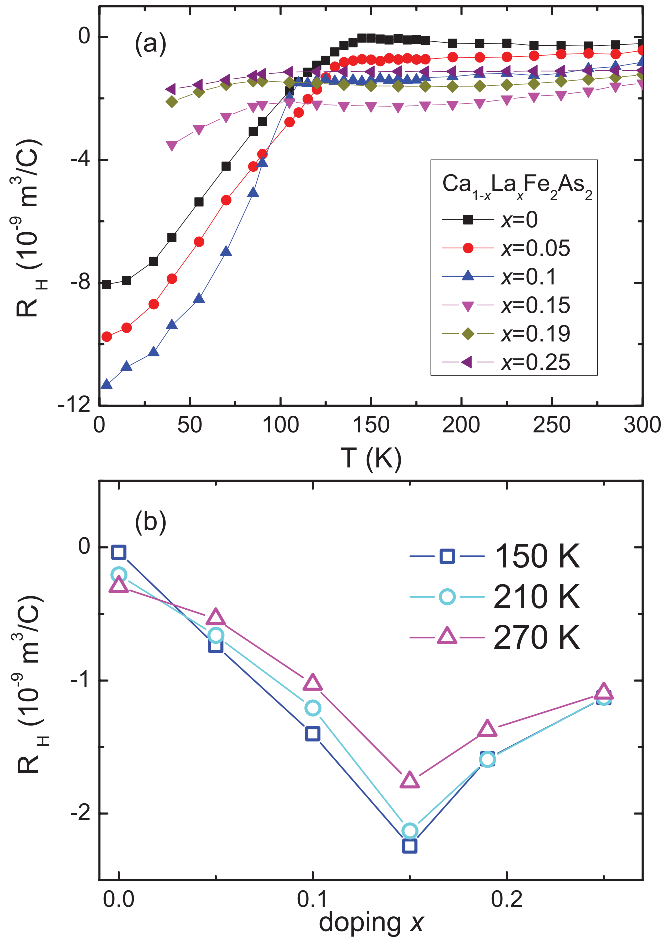

FIG. 4. (Color online) (a) Temperature dependence of R_H for $Ca_{1-x}La_xFe_2As_2$. (b) Doping dependence of R_H at certain temperature in the normal state.

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