Transport and magnetic properties of La-doped CaFe$_2$As$_2$

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We measured the transport properties and susceptibility of single crystals Ca$_{1-x}$La$_x$Fe$_2$As$_2$ (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 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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Iron-based superconductors have attracted great attentions these years $^{1,2}$. 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$_2$As$_2$ ($A$=Ca, Sr, Ba, Eu, so called "122") with the ThCr$_2$Si$_2$-type structure were widely investigated because it is easy to grow 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$_2$As$_2$ $^{3,4}$. The FeAs plane of Ca$_{1-x}$R$_x$Fe$_2$As$_2$ ($R$=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$_x$As$_2$ and K$_x$Fe$_{2−y}$Se$_2$, some of the Fe ions in the FeAs/FeSe layers are either substituted by Co or missing $^{2,11}$. 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$_x$Fe$_2$As$_2$ is much higher compared to the other 122 iron pnictides and it is very necessary for us to detailedly investigate the physical properties of Ca$_{1−x}$R$_x$Fe$_2$As$_2$.

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$_x$Fe$_2$As$_2$, in-plane resistivity anisotropy is nearly absent $^{16}$. All the previous works were focusing 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$_x$Fe$_2$As$_2$ with the perfect Fe square lattice. The large in-plane anisotropy observed in Ca$_{1−x}$R$_x$Fe$_2$As$_2$ in this paper indicates that the large in-plane resistivity anisotropy is related to the electron-doping rather than transition metal doped in the FeAs plane.

In this paper, we systematically investigated the transport and magnetic properties of La-doped CaFe$_2$As$_2$. Superconductivity up to 43 K was observed in the Ca$_{0.81}$La$_{0.19}$Fe$_2$As$_2$ similar to the previous results $^{2}$. SDW transition can be suppressed through La doping and superconductivity coexists with antiferromagnetic with 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.

High quality single crystals with nominal composition Ca$_{1−x}$La$_x$Fe$_2$As$_2$ (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 $^{2,12}$. 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 plate-like Ca$_{1−x}$La$_x$Fe$_2$As$_2$ crystals were mechanically cleaved from the flux and obtained for measurements. The actual composition of the single crystals were characterized by the 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 with the previous work\textsuperscript{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. \( \rho_a \) (current parallel to a) and \( \rho_b \) (current parallel to b) were measured on the same sample using standard 4-point configuration.

Single crystals of Ca\(_{1-x}\)La\(_x\)Fe\(_2\)As\(_2\) were characterized by x-ray diffractions (XRD) using Cu \( K_a \) radiations. As shown in the Fig.1(a). Only (00l) 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 c-axis almost do not change with La doping. The lattice constant of c-axis was around 11.72 \( \AA \) for all the samples. It is slightly different from the polycrystalline samples reported previously for which the c-axis slightly decrease with rare earth elements doping\textsuperscript{2}. Fig.1(b) shows the temperature dependence of the resistivity with the current flowing along a direction and b direction respectively for (a): parent compound CaFe\(_2\)As\(_2\), (b): Ca\(_{0.95}\)La\(_{0.05}\)Fe\(_2\)As\(_2\), (c): Ca\(_{0.9}\)La\(_{0.1}\)Fe\(_2\)As\(_2\). The twinned in-plane resistivity was also shown for comparison (blue line). (d): Temperature dependence of in-plane resistivity anisotropy \( \rho_b/\rho_a \). The insets of (f) are the Polarized-light images of the surface for twinned(i) and detwinned(ii) CaFe\(_2\)As\(_2\) at the temperature of 78 K.

FIG. 1: (Color online)(a): The single crystal x-ray diffraction pattern of Ca\(_{1-x}\)La\(_x\)Fe\(_2\)As\(_2\). Only (00l) 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.
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 Curie-Weiss behavior in the low temperature.

$T_{SDW}$. With increasing La doping level, the in-plane resistivity anisotropy gradually increases in the SDW region. It is very similar with the other underdoped electron-doping 122 systems, but quite different from the hole-doped Ba$_{1-x}$K$_x$Fe$_2$As$_2$. 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$_x$Fe$_2$As$_2$ ($x=0$, 0.05 and 0.1) with magnetic field of $H=1T$ applied along the ab-plane are shown in Fig.3 (a). The susceptibility of parent compound CaFe$_2$As$_2$ 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 with the previous result. Small amount doping of La obviously enhances the Curie-Weiss-like behavior at low temperature. With increasing the doping content, the anomaly due to SDW order is gradually suppressed and T-linear behavior of susceptibility is gradually broken due to the Curie-Weiss-like behavior at low temperature. It strongly contrast to Co-doped 122 samples in which the T-linear behavior of susceptibility survives with Co doping. With further increasing 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$_x$Fe$_2$As$_2$ is strongly different to the other 122 iron-pnictide superconductors.

Fig.4(a) shows the temperature dependence of Hall coefficient $R_H$ of Ca$_{1-x}$La$_x$Fe$_2$As$_2$. $R_H$ of all the samples show the negative values, indicating that the dominated carrier is 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. It is also instructive to analyze the Hall Coefficient at certain temperature 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 RH increases with increasing the doping content. With further doping, it gradually decreases. This behavior is quite similar to the BaFe2−xCo2As2 system. Such behavior is caused by the multiband effect and different mobility of electron or hole carriers.

Large in-plane anisotropy is observed in the underdoped region of Ca1−xLaxFe2As2 although no extra elements were introduced into the FeAs-plane. It strongly contrasts to the hole-doped Ba1−xKxFe2As2 system, but is similar to the transition metal substitution samples. Our results show that substitution away from the FeAs plane could also lead to large in-plane anisotropy, which indicate 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 the orbital degree of freedom or and spin fluctuations. Our previous work demonstrates that the microscopic orbital involvement in magnetically ordered state must be fundamentally different between the hole and electron underdoped iron pnictides. Large in-plane anisotropy observed in rare earth doped materials also prove this. ARPES experiments need to do to compare the orbital characters of the hole and electron doped samples. The magnetic susceptibilities of Ca1−xLaxFe2As2 show much stronger Curie-Weiss-like behavior compared to the other 122 iron pnictide superconductors. Although superconductivity above 40K was observed in this system which is much higher than the other 122 superconductors, superconducting transition is broad. The origins of the strong Curie-Weiss-like behavior and broad superconducting transition in this system are still unknown.

In conclusion, we systematically measured the transport properties and susceptibilities of Ca1−xLaxFe2As2 (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 iron-pnictides, but strongly contrasts to the hole-doped Ba1−xKxFe2As2. Strong Curie-Weiss-like behavior of susceptibility was observed at low temperature by increasing the La doping.

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