Doping Dependence of Superconductivity and Lattice Constants in Hole Doped 
$La_{1-x}Sr_xFeAsO$

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By using solid state reaction method we have fabricated the hole doped $La_{1-x}Sr_xFeAsO$ superconductors with Sr content up to 0.13. It is found that the sharp anomaly at about 150 K and the low temperature upturn of resistivity are suppressed by doping holes into the parent phase. Interestingly both the superconducting transition temperature $T_c$ and the lattice constants (a-axis and c-axis) increase monotonously with hole concentration, in sharp contrast with the electron doped side where the $T_c$ increases with a continuing shrinkage of the lattice constants either by dope more fluorine or oxygen vacancies into the system. Our data clearly illustrate that the superconductivity can be induced by doping holes via substituting the trivalent La with divalent Sr in the LaFeAsO system with single FeAs layer, and the $T_c$ in the present system exhibits a symmetric behavior at the electron and hole doped sides, as we reported previously.

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The discovery of superconductivity at 26 K in iron-based layered quaternary compound $LaFeAsO_{1-x}F_x$ [1] has generated enormous efforts. This iron-based system attracts a lot of attention since it may have an unconventional superconducting mechanism as well as potential applications. Normally the Fe or Ni elements form the materials with long range ferromagnetic order which is detrimental to the spin singlet superconductivity, but it seems to be an exception in this iron-based system. Many new high temperature superconductors were then discovered and the superconducting transition temperature has been quickly raised to $T_c = 55$ K in SmFeAsO$_{0.9}F_{0.1}$ [2]. So far most of the discovered superconductors are categorized into the so-called electron doped side, while in $La_{1-x}Sr_xFeAsO$ superconductivity with $T_c = 25$ K [3] was discovered by substituting La with Sr and assumed to be the first hole doped superconductor in the iron-based system. Positive Hall coefficient $R_H$ measured in these hole doped samples well confirmed that the conduction is through hole-like charge carriers. The discovery of the hole doped superconductors in the new system puts a lot of constraints on the theoretical picture to understand the superconducting mechanism. Later on superconductivity at about 38 K was found in $Ba_{1-x}K_xFe_2As_2$ [4]. This has been repeated by many other groups by trying to replace the Ba site with Sr and K site with Cs etc. [5, 6, 7, 8] and the Hall effect data have also evidenced that they are hole doped superconductors.

In this paper we present a systematic study on the evolution of the superconductivity and the lattice constants with the content of Sr in $La_{1-x}Sr_xFeAsO$. A close and intimate relationship between the lattice constants and the superconducting transition temperature has been found in the hole doped side: they both increase monotonously with doped concentration of Sr. Our data and analysis can also give an explicit explanation to the recent report by Wu et al. [9] that they did not observe bulk superconductivity in a nominally 15% Sr doped as-grown sample $La_{0.85}Sr_{0.15}FeAsO_{1-\delta}$. After having a detailed analysis, we found that their so-called as-grown sample resided actually at a Sr concentration of about $4 \pm 1\%$, far below 15% in the nominal composition as they believed. This prevents them to see the superconductivity up to 26 K in a higher hole doping level. Our results clearly illustrate that the bulk superconductivity in the LaFeAsO system can be induced by hole doping.

We employed a two-step solid state reaction method to synthesize the $La_{1-x}Sr_xFeAsO$ samples. In the first step, LaAs and FeAs were prepared by reacting grains of La (purity 99.99%), Fe powder (purity 99.95%) and As grains (purity 99.99%) at 500 °C for 8 hours and then 700 °C for 10 hours. They were sealed in an evacuated quartz tube when reacting. Then the resultant precursors were thoroughly ground together with Fe powder (purity 99.95%), Fe$_2$O$_3$ powder (purity 99.5%) and SrCO$_3$ powder (purity 99.9%) in stoichiometry as given by the formula $La_{1-x}Sr_xFeAsO$. Therefore our samples are not oxygen deficient from the starting materials. The oxygen is even more than that in the stoichiometric formula if counting the oxygen carried by CO$_2$. Sometime we also use SrO instead of SrCO$_3$ to make the superconductors successfully. The obtained mixtures were pressed into pellets and sealed in a quartz tube with high vacuum. Ar gas is not needed in the quartz tube because CO$_2$ gas was produced during the reaction. The materials were then heated up to 1150 °C with a rate of 200 °C/hr and maintained for 40 hours. Then a cooling procedure with a rate of 100 - 200 °C/hr was followed. We found that it is necessary to bake the starting materials Fe$_2$O$_3$ and SrCO$_3$ at 350°C for hours ahead of the synthesizing process in order to remove the moisture absorbed by the powder. This baking seems very essential to have samples with superconductivity when handling the materials in a humid environment. We also found that using Ta...
foil to wrap the sample during the sintering should be strictly avoided since it reacts with some components of the materials, probably with FeAs and SrCO$_3$. The Ta foil will become dark and brittle if it is used.

In Fig.1(a) we present a typical set of resistive data for the sample $La_{0.9}Sr_{0.1}FeAsO$ with $x=0.1$, it has an onset transition temperature of about 25 K. Fig.1(b) shows the diamagnetic transition measured on the same sample with AC susceptibility technique. An estimation on the magnetic signal tells that the superconducting shielding volume of the sample is beyond 60%. Samples with this kind of transitions can be easily repeated by carefully following the synthesizing procedures we provided above. Our result is in sharp contrast with that of Wu et al.[9], they did not see bulk superconductivity in $La_{1-x}Sr_xFeAsO$ with $x=0.15$, but rather the resistivity exhibits a strange behavior in the normal state with a tiny superconducting-like drop of resistivity at about 5 K. Our impression about their as-grown sample is that the true Sr content in these samples is indeed very low and they are still close to the undoped parent phase as suggested by the large resistivity anomaly at about 150-160 K.

In the main frame of Fig.2 we show the resistivity data of our samples made at various doping levels of Sr ranging from $x=0.02$ to 0.13. One can see that by using only 2% doping of Sr, the upturn of resistivity in the low temperature region has been clearly suppressed, and the resistivity anomaly at about 150 K becomes rounded compared to the parent phase.[10] Up to 4% doping, both effects are suppressed strongly and a tiny resistivity drop which may be due to superconductivity can be seen. At a doping level of 8%, a superconducting transition with onset point of 19.6 K occurs. At the doping level of 0.10-0.13, the superconductivity becomes optimal with a onset transition of 0.13, which was wrapped by a Ta foil during the high temperature sintering (see text).

![FIG. 1: (Color online) Temperature dependence of resistivity for the $La_{0.9}Sr_{0.1}FeAsO$ sample. A flattening of resistivity in high temperature part is obvious, which seems to be a common feature of the hole doped iron-based superconductors. (b) The AC susceptibility of the same sample measured with $H_{ac} = 0.1$ Oe, $f=333$ Hz.](image1)

![FIG. 2: Temperature dependence of resistivity of samples $La_{1-x}Sr_xFeAsO$ with $x = 0.02$, 0.04, 0.08, 0.10, 0.13. One can see that the resistivity anomaly and the low temperature upturn are suppressed by doping more Sr into the system. The superconductivity appears eventually. Inset: A typical resistivity curve measured on a sample with nominal composition of 0.13, which was wrapped by a Ta foil during the high temperature sintering (see text).](image2)
and eventually the superconductivity sets in. This is just like that in the double layer system \( Ba_{1-x}K_x(FeAs)_2 \), introducing holes into the sample by substituting \( Ba \) with \( K \), the spin-density-wave like order in the parent phase will be suppressed and finally superconductivity wins out of the ground state.

In order to have a comprehensive understanding to the evolution induced by the doping process, we have measured the X-ray diffraction patterns for all samples. The lattice constants of \( a \)-axis and \( c \)-axis are thus obtained. It is known that the lattice constants (both \( a \)-axis or \( c \)-axis) will decrease with either fluorine doping or more oxygen deficiency in \( LaFeAsO \). This has been supposed to be an effective way to increase \( T_c \) in the iron-based system. In Fig.3 we present the XRD patterns for five selected samples. For clarity, the XRD data of samples with other doping levels are not included here. It is clear that all main peaks of the samples can be indexed to the tetragonal ZrCuSiAs-type structure, leading to the determination of the lattice constants. An enlarged view on the (102) peak for all samples clearly illustrate a systematic evolution: the peak shifts monotonously to the left-hand side direction in the order of 10\% F-doped \( LaFeAsO \), undoped \( LaFeAsO \) and then \( La_{1-x}Sr_xFeAsO \). For the \( Sr \) doped \( La_{1-x}Sr_xFeAsO \) samples, the peaks also shift to more left-hand side with more \( Sr \) concentration, indicating larger lattice constants. This is reasonable since the radii of \( Sr^{2+} \) is about 1.12 ˚A, which is larger than that of \( La^{3+} \) of about 1.06 ˚A. The systematically expanded lattice constants with \( Sr \) doping strongly suggest that \( Sr \) atoms go into the lattice structure of \( LaFeAsO \).

Next we have a close look at the doping dependence of the lattice constants and the superconducting transition temperature \( T_c \), as shown by Fig.4. It is clear that both the \( a \)-axis and \( c \)-axis lattice constants expand monotonously starting from 10\% F-doped sample, the undoped \( LaFeAsO \) sample, and the \( Sr \) doped samples. Interestingly the onset superconducting transition temperature increases towards either more hole doped or electron doped side. This strongly suggests that the \( T_c \) may have a symmetric behavior in both sides as suggested in our earlier paper. If we put the lattice constants from the samples of Wu et al. onto our plots, one can see that they reside quite close to the undoped case. This is in consistent with the resistive transition curve which shows a tiny drop of resistivity at about 5 K which may be induced by the superconductivity in hole doped side. In addition, this argument is further corroborated by the fact that their as grown sample has a strong resistivity anomaly as the undoped sample, together with the slight positive thermoelectric power, but still negative Hall coefficient. If we further put their data points of the vacuum annealed samples together, more interesting physics emerges: the system was driven to the electron doped side again and finally a superconductivity at about 26 K was observed with a sample annealed for 4 hours. The lattice constants of these two annealed samples follow also roughly well with the general tendency, i.e., they drop down when \( T_c \) is increased towards more electron doping. Above discussion indicate that the as-grown sample of Wu et al. is actually slightly hole doped although the nominal \( Sr \) composition is 0.15. This prevents them to observe the superconductivity up to 26 K in more hole doped samples as seen in our experiments. However, an interesting point arises from their annealed samples is that the system can be driven completely back to the electron doped side by having the annealing in high vacuum and at a high temperature.

To further support our argument, we have measured the Hall resistance of the hole doped sample with \( x = 0.1 \) (the same one shown in Fig.1). Fig.5 presents the data of Hall effect measurements. It is clear that the Hall resistance is positive in wide temperature region. An interesting discovery which was reported in our previous paper as well as in the recent papers in \( (Ba, Sr)_{1-x}K_x(FeAs)_2 \) is that the Hall coefficient \( R_H \) has a huge bump in the low temperature region, but it gradually becomes very small and changes sign at a even high temperature. This seems to be another common feature in hole doped iron-based superconductors. When having a combined look at both Fig.2 and Fig.5, it is found that the hump of Hall coefficient \( R_H \) vanishes at
FIG. 4: (Color online) Doping dependence of (a) a-axis lattice constant; (b) c-axis lattice constant; (c) the onset superconducting transition temperature. Filled squares are data from our measurements. For electron doped side, the variable “x” represents the fluorine concentration or the similar electronic state by doping oxygen vacancies. The red filled circles represent the lattice constants and $T_c$ from the work of Wu et al.\cite{3} if we put their results on our general lines. The open squares roughly tell the positions of the two samples of Wu et al.\cite{9} if we put their results on our general lines. The vertical dotted line indicates the undoped position.

about 200 K where the normal state resistivity flattens out. This coincidence may suggest that the two common features in the hole doped iron-based superconductors have the same origin. The positive Hall coefficient $R_H$ as well as the close similarity with other two-layer hole doped system $Ba_{1-x}K_x(FeAs)_2$ make our Sr doped samples $La_{1-x}Sr_xFeAsO$ well footed on the category of hole doped superconductors. Similar substitution with other rare earth elements are worthwhile to try and may generate new superconductors with higher $T_c$.

In summary, a systematic evolution of superconductivity and the lattice constants in hole doped $La_{1-x}Sr_xFeAsO$ has been discovered. By doping more Sr into the parent phase $LaFeAsO$, the low temperature upturn and the sharp anomaly at about 150 K of resistivity are suppressed and the superconductivity eventually sets in. The superconducting transition temperature as well as the lattice constants increase monotonously with Sr concentration up to $x = 0.13$ where $T_c = 26$ K. Together with the positive Hall coefficient $R_H$ and the similar temperature dependence with other hole doped iron-based superconductors, we conclude that the superconductivity can be induced by either hole doping (through substitution of La by Sr) or electron doping (through substitution of oxygen by fluorine, or by inducing oxygen vacancies) in the single layer system $LaFeAsO$.

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FIG. 5: (Color online) Temperature dependence of Hall coefficient $R_H$ determined on the sample $La_{0.5}Sr_{0.5}FeAsO$. A huge bump appears in the low temperature region, which seems to be a common feature for all hole doped superconductors. Inset: The raw data of the Hall resistivity $\rho_{xy}$ at different temperatures.

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[1] Y. Kamihara et al., J. Am. Chem. Soc. 130, 3296 (2008).
[2] Z. A. Ren et al., Chin. Phys. Lett. 25, 2215 (2008).
[3] H. H. Wen et al., Europhys. Lett. 82, 17009 (2008).
[4] M. Rotter et al., arXiv:cond-mat/0805.4630.
[5] C. Krellner et al., arXiv:cond-mat/0806.1043.
[6] G. F. Chen et al., arXiv:cond-mat/0806.1209.
[7] K. Sasmal et al., arXiv:cond-mat/0806.1301.
[8] G. Wu et al., arXiv:cond-mat/0806.1459.
[9] G. Wu et al., arXiv:cond-mat/0806.1687.
[10] J. Dong et al., arXiv:cond-mat/0803.3426.
[11] Z. A. Ren et al., Europhys. Lett. 83, 17002 (2008).
[12] T. Watanabe et al., arXiv:cond-mat/0805.4340.