Superconductivity at 25 K in hole doped $(La_{1-x}Sr_x)OFeAs$

Hai-Hu Wen*, Gang Mu, Lei Fang, Huan Yang, and Xiyu Zhu

National Laboratory for Superconductivity, Institute of Physics and Beijing National Laboratory for Condensed Matter Physics, Chinese Academy of Sciences, P. O. Box 603, Beijing 100080, People's Republic of China

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Abstract. - By partially substituting the tri-valence element La with di-valence element Sr in $LaOFeAs$, we introduced holes into the system. For the first time, we successfully synthesized the hole doped new superconductors $(La_{1-x}Sr_x)OFeAs$. The maximum superconducting transition temperature at about 25 K was observed at a doping level of x = 0.13. It is evidenced by Hall effect measurements that the conduction in this type of material is dominated by hole-like charge carriers, rather than electron-like ones. Together with the data of the electron doped system $La(O_{1-x}F_x)FeAs$, a generic phase diagram is depicted and is revealed to be similar to that of the cuprate superconductors.

Introduction. – Superconductivity is a quantum phenomenon that shows the vanishing of resistivity and exclusion of magnetic field due to the condensation of paired electrons. A discovery of high temperature superconductors not only brings about enormous scientific interests, but also leads to potential applications. Besides the high temperature superconductivity in the cuprate system that was firstly found in 1986 [1], and that in MgB_2 found in 2001 [2], efforts in exploring new materials lead to the discovery of superconductivity in many other systems, such as $Na_xCoO_2 \cdot 1.3H_2O$ [3], Sr_2RuO_4 [4] and etc., but all these have the transition temperatures below 20 K. Searching new superconductors with 3d or 4d transition metal compounds is specially interesting since the relatively strong localization effects of electrons in these materials quite often lead to strong correlation effects. In 1995, the fabrication of a series of quaternary oxypnictides in a general formula as LnOMP (where Ln= La-Nd, Sm and Gd; M = Mn, Fe, Co, Ni and Ru) was published [5]. The system has a layered structure and a tetragonal P4/nmm space group, with a stacking series of $-(LnO)_2-(MP)_2-(LnO)_2-$. In one unit cell, there are two molecules of LnOMP, and it is valence self-balanced, i.e., $(LaO)^{+1}$ is balanced by $(MP)^{-1}$. Some of them, such as LaOFeP and LaONiP, were shown to be superconductors at about 4 K [6] and 3 K [7], respectively. By substituting the oxygen with F, the T_c was increased to 7 K [6]. These iron based materials constructed a new family of layered superconductors without copper. Very recently, Kamihara et al. [8] found that by substituting P with As, and by substituting partially the O in LaOFeP with F, the resultant material $La(O_{1-x}F_x)FeAs$ (x = 0.05 to 0.12) became superconductive at 26 K. This is really surprising since the iron elements normally give rise to magnetic moments, and in many cases they form a long range ferromagnetic order, and are thus detrimental to the superconductivity with singlet pairing. This interesting discovery has already attracted intense efforts [9–13] both from experimental and theoretical side. Since the substitution of O^{2-} by F^- can introduce more electrons into $LaOFeAs$, it was called as electron-doped. Interestingly, by substituting La^{3+} with Ca^{2+} which brings more holes into the system, Kamihara et al. [8] found no trace of superconductivity and suggested that: a critical factor for induction of superconductivity in this system is electron doping, and not hole doping. In this Letter, we show the evidence of superconductivity in $LaOFeAs$ achieved by substituting La^{3+} with Sr^{2+}, that is through hole doping. The highest transition temperature found here is about 25 K.

Sample preparation and experiment. – By using a two-step method, we successfully fabricated the $(La_{1-x}Sr_x)OFeAs$ (x = 0.10 - 0.30) and $La(O_{0.9}F_{0.1-\delta})FeAs$ [13] samples. First the starting materials Fe powder (purity 99.95%) and As grains (purity 99.99%) were mixed in 1:1 ratio, grounded and pressed into a pellet shape. Then it was sealed in an evacuated quartz tube and followed by burning at 700 °C for 10 hours. The resultant pellet was smashed and grounded together with the $SrCO_3$ powder (purity 99.9%), La_2O_3 powder (purity 99.9%) and grains of La (purity 99.99%) in stoichiometry as the formula $(La_{1-x}Sr_x)OFeAs$. Again it was pressed into a pellet and sealed in an evacuated quartz tube and burned at about 900-940 °C for 4 hours, followed by a burning at 1150-1200 °C for 48 hours. Then it was cooled down slowly to room temperature. In Fig. 1(a), we show the X-ray diffraction (XRD) patterns for the sample $(La_{0.87}Sr_{0.13})OFeAs$. It is found that the peaks from XRD are dominated by the phase of $LaOFeAs$ for low doping (below about x=0.15) although some impurity peaks appear also. Beyond that doping, some strong peaks from the impurity phase emerge and are getting stronger with more doping. But the XRD taken from all samples gives clear evidence that the main peaks are from the phase $(La_{1-x}Sr_x)OFeAs$. From Fig. 1(a), it is clear that almost all main peaks can be indexed by a tetragonal structure with $a = b = 4.0350\mathring{A}$ and $c = 8.7710\mathring{A}$. These lattice constants are a bit larger than those in the parent phase $LaOFeAs$ ($a = b = 4.032\mathring{A}$ and $c = 8.726\mathring{A}$), suggesting that the lattice expands a bit with Sr substitution, especially along the c-axis. This is understandable since the radius of Sr^{2+} is $1.12\mathring{A}$ which is larger than that of La^{3+} (1.06 $\mathring{A}$). Therefore, it is certain that the dominant component is from $(La_{0.87}Sr_{0.13})OFeAs$. There are several peaks marked by the asterisks which may come from the impurity phase of FeAs and LaAs. In Fig. 1(b) we present the energy dispersive x-ray microanalysis (EDX) spectrum of one typical grain, which shows that the main elements of the grains are La, Sr, Fe, As and O. It is thus safe to conclude that the superconductivity observed here comes from the main phase $(La_{1-x}Sr_x)OFeAs$.

The magnetic measurements were done with a superconducting quantum interference device (Quantum Design, SQUID, MPMS7), and an Oxford cryogenic system Maglab-12T. The AC susceptibility of the samples were measured with the Maglab-12T with an AC field of 0.1 Oe and a frequency of 333 Hz. The superconductivity was also proved by the DC magnetization measurements using the zero-field-cooled mode, that is by cooling the sample at zero field to 2 K, then applying a magnetic field and the data was collected during the warming up process. The resistivity and Hall effect measurements were done with a physical property measurement system (Quantum Design, PPMS9T) with a six-probe technique. The current direction was changed for measuring each point in order to remove the contacting thermal power.

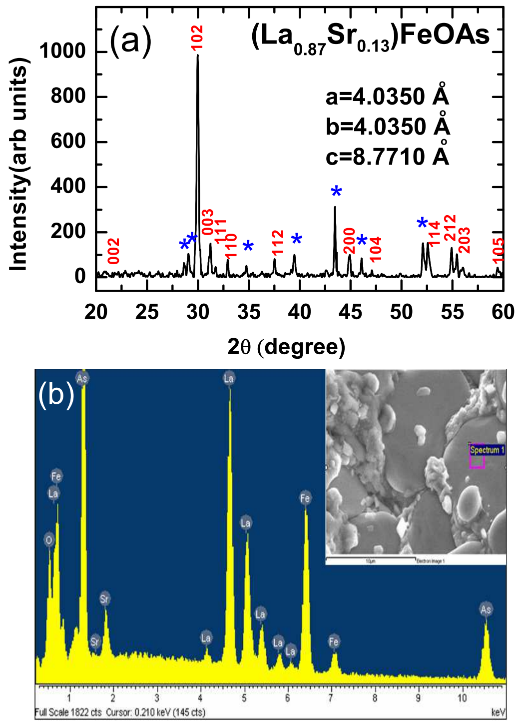

Fig. 1: (a) X-ray diffraction patterns for the sample $(La_{0.87}Sr_{0.13})OFeAs$. All main peaks can be indexed by a tetragonal structure with $a = b = 4.0350\mathring{A}$ and $c = 8.7710\mathring{A}$, indicating that the dominant phase here is $(La_{0.87}Sr_{0.13})OFeAs$. The asterisks mark the peaks from the impurity phase. (b) The EDX spectrum taken from one of the the main grains, which shows that the main elements of the grains are La, Sr, Fe, As and O. The inset in (b) shows a scanning electron microscopic picture. The little rectangle marks the position where we took the EDX spectrum.

Results and discussion. – In Fig.2 (a) we present the temperature dependence of the resistive transitions for samples $(La_{1-x}Sr_x)OFeAs$ with x = 0.10 to 0.20. One can see that the onset transition temperature taken with a criterion of 95% ρ_n shifts slowly to higher values with the doping amount of Sr from 0.10 to 0.13. The maximum onset $T_c \approx 25.6$ K is achieved at a doping of x = 0.13 and the zero resistance temperature is about 15 K. Then onset T_c drops down slowly with further doping and becomes zero at the doping level of about 0.23. This doping dependence is quite similar to that in electron doped samples $La(O_{1-x}F_x)FeAs$ where the T_c is rather stable in the middle doping regime (x = 0.05 to 0.11). This flattening behavior of T_c is very different from that in cuprate superconductors in which a parabolic doping dependence was observed. At this moment, our samples are not pure enough, therefore the transitions are still broad, and the T_c values determined here may change in the clean or pure samples. Thus the rather stable T_c versus doping may be an intrinsic effect of the material, or it may be induced by the inhomogeneous phase formed during the reaction. In Fig.2 (b) the resistivity in wide temperature region is shown for the same samples. A huge bump appears for all samples in high temperature region, which may reflect an unusual electron scattering process or a drastic change of electron phonon scattering. We will see later that, just

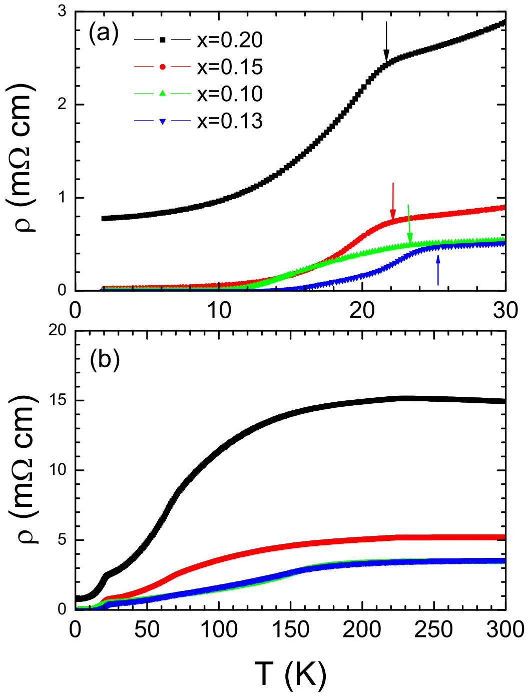

Fig. 2: The temperature dependence of resistivity of samples $(La_{1-x}Sr_x)OFeAs$ with the Sr concentration x changing from 0.10 to 0.20. One can see that the onset transition temperatures marked here by arrows are quite close to each other, with the highest $T_c \approx 25.6K$ at the doping of 0.13. Beyond x = 0.20, no superconductivity was observed.

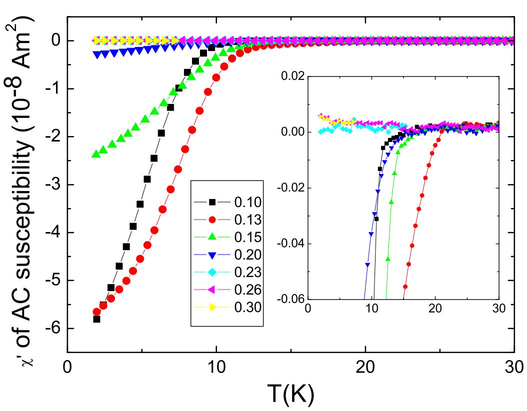

Fig. 3: The temperature dependence of the real part of the AC susceptibility measured with an AC field of 0.1 Oe and the oscillating frequency of 333 Hz. The inset shows an enlarged view of the same data in the main frame, with also the same coordinates. The onset transition temperature behaves in the same way as that determined from the resistivity data.

corresponding to the appearance of this bump, the Hall coefficient drops down quickly. This huge bump appears for all samples here, which may have the same origin as that appearing in the electron doped samples as marked as T_{anom} in [8]. By increasing the doping level, the general resistivity gets larger. This is an interesting behavior, again we are not sure whether this is an intrinsic effect of the $(La_{1-x}Sr_x)OFeAs$ phase, or it is due to an extrinsic effect, such as much stronger impurity scattering by more impurity centers at a high doping level. This remark may be true since the sample x = 0.20 with larger normal state resistivity has not come into the complete superconducting state even when the temperature goes down to 2 K.

In Fig.3 we show the temperature dependence of the dia-magnetization measured using AC susceptibility based on an Oxford cryogenic system Maglab-12T. Although the transitions are still broad, an enlarged view shown in the inset allow us to determine the onset magnetic transition point. It is known that the magnetic onset transition point is normally close to the resistive transition point at 50-90% ρ_n. Therefore the magnetic onset T_c values determined in this way are a bit lower than that determined from the onset transition of resistivity. But it is clear that the onset transition temperature determined on the magnetic signal follows the same way as the resistive data. Both the resistive and magnetic transition curves are still not perfectly sharp, which leaves more room for improving the sample quality in the future work. But this does not give any doubt about the superconducting transition temperatures determined here. It is worthy to mention that, as reported in the original paper for the electron doped samples [8], a magnetic background appears for all samples investigated here. The magnetization-hysteresis-loop measurements above T_c indicate that it has a weak ferromagnetic feature. We don't know whether this magnetic signal is an intrinsic property of the $LaOFeAs$ phase, or it is due to the impurity phase. If the former case is true, the superconductivity in the present system should be categorized as a non-conventional one.

In order to know whether the Sr doped samples are really in the hole doped regime, we measured the Hall effect for all the samples. As an example, in Fig. 4(a) we show the Hall resistivity ρ_{xy} for both $(La_{0.87}Sr_{0.13})OFeAs$ and the electron doped sample $La(O_{0.9}F_{0.1})FeAs$. It is clear that ρ_{xy} is positive at all temperatures below 200 K for $(La_{0.87}Sr_{0.13})OFeAs$ leading to a positive Hall coefficients $R_H = \rho_{xy}/H$. This is in sharp contrast with the data of the electron doped sample $La(O_{0.9}F_{0.1})FeAs$ [13]. The positive Hall resistivity appears for all Sr-doped samples. In Fig. 4(b) the temperature dependent Hall coefficient of the two samples are shown. One can see that the Hall coefficient for the hole doped sample has much stronger temperature dependence, which may suggest a stronger multiband effect in the present sample. In addition, beyond about 200 K, the Hall coefficient drops to zero and becomes even slightly negative. This change is just corresponding to the appearance of the huge bump on the

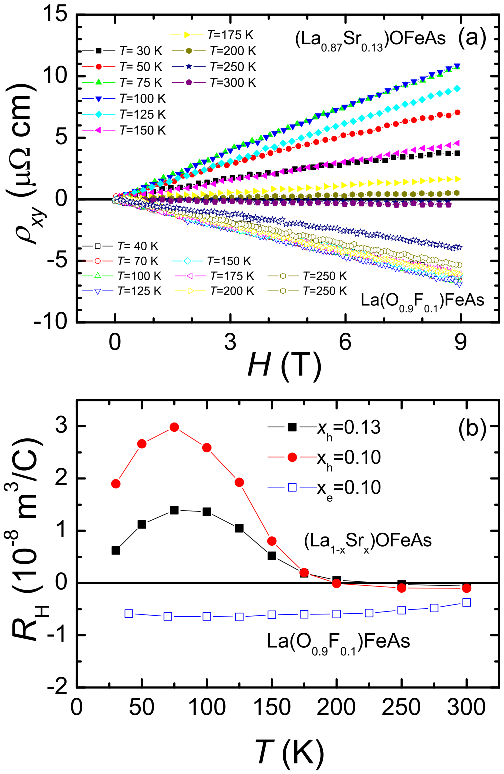

Fig. 4: Hall effect measurements for one sample $(La_{0.87}Sr_{0.13})OFeAs$ in present work and an electron doped sample $La(O_{0.9}F_{0.1})FeAs$. (a) Magnetic field dependence of Hall resistivity ρ_{xy} of the two samples, filled symbols for $(La_{0.87}Sr_{0.13})OFeAs$, open symbols for $La(O_{0.9}F_{0.1})FeAs$. One can see that the Hall resistivity is positive for the sample $(La_{0.87}Sr_{0.13})OFeAs$ in wide temperature regime, which is in sharp contrast with that of $La(O_{0.9}F_{0}.1)FeAs$. (b) The temperature dependence of the Hall coefficient R_H taking in the zero field approach for the two samples, filled symbols for $(La_{0.87}Sr_{0.13})OFeAs$, open symbols for $La(O_{0.9}F_{0.1})FeAs$. This result clearly indicates that our present sample has hole-like charge carriers for the electron conduction in wide temperature region. But a much stronger temperature dependence was observed which may suggest a stronger multiband effect in the hole doped samples.

resistivity curve in the same temperature region. Interestingly, in the electron doped samples, the Hall coefficient also drops down when a little saturation of resistivity occurs. [13]. This similarity may indicate an intimate connection between these two different samples. It is clear that, in wide temperature region, the Hall coefficient of the two samples has different signs. The magnitudes of R_H for the two samples at about 100 K are in the same scale. If using the single band equation $n = 1/R_H e$ to evaluate the charge carrier density, at 100 K, we obtained $n(electron - doped) = 9.8 \times 10^{20}/cm^3$, while $n(hole-doped) = 4.57 \times 10^{20}/cm^3$, both have a low

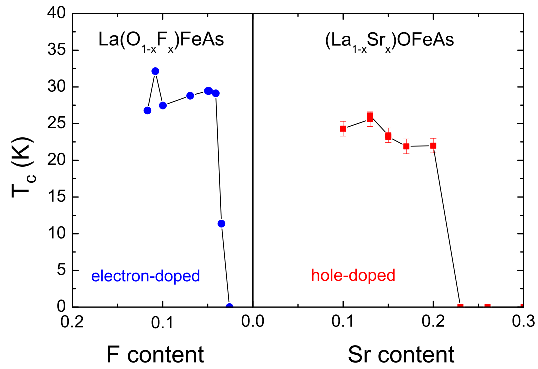

Fig. 5: The generic phase diagram depicted based on the data of our present system $(La_{1-x}Sr_x)OFeAs$ and that of electron doped system $La(O_{1-x}F_x)FeAs$. The phase diagram looks very similar to that of cuprate superconductors.

charge carrier density. This may give support to a theoretical proposal that the iron based superconductor has very low superfluid density. [9] The positive sign of Hall coefficient in our present Sr doped samples convinces us that they are indeed hole doped. We also tried to substitute La with Ca at a concentration of 0.1, the result is the same as that reported by Kamihara et al. [8], that is no superconductivity was found. Therefore it leaves a very interesting argument that the superconductivity is not only controlled by the property of the $FeAs$ layer, but also strongly influenced by the LaO layer with a subtle change.

Finally, in Fig.5, we depict a generic phase diagram by combining our data from the hole doped system $(La_{1-x}Sr_x)OFeAs$ and the data from the electron doped system $La(O_{1-x}F_x)FeAs$ of Kamihara et al. [8]. Besides the somewhat flattened doping dependence of T_c in the intermediate doping regime, interestingly, the phase diagram looks very similar to that of the cuprates, which may give important clues to the mechanism of cuprate superconductors. At this moment, we don't know whether there is also a pseudogap in the normal state of the present iron-based superconductors as appearing in underdoped cuprates [14]. A detailed investigation on the properties of the hole doped samples at different doping levels in present system is highly desired. The similarity between the phase diagrams of the cuprates and the iron-based system may imply that the superconductivity is in the vicinity of some magnetic correlations, such as an antiferromagnetic correlations/fluctuations in the cuprates, and ferromagnetic correlations/fluctuations in the present iron-based materials. This argument can get a support if the magnetic signal with a weak ferromagnetic feature in the normal state is intrinsic to the $LaOFeAs$ system. Regarding the superconductivity found in the hole doped side, and combining the density of states calculated by Dynamical Mean Field Theory (DMFT) [11], we suggest that the $3d_{xy}$ orbit may paly an important role here. The new phase diagram for this iron-based superconducting system without copper may open a new era for the research of fundamental mechanism of superconductivity, which will probably promote the solution to the mechanism of cuprate superconductors. Our discovery of superconductivity in the hole doped side will widely open the territory for exploring new superconductors, hopefully leading to a much higher superconducting transition temperature.

Conclusion. – In summary, by substituting the trivalence element La partially by di-valence element Sr in LaOFeAs, we introduced holes into the system and found superconductivity. The maximum transition temperature is about 25 K at a doping level of x = 0.13. The resistive onset transition temperature is rather stable in wide doping region from 0.10 to 0.20, but no superconductivity was observed beyond x = 0.23. Evidence for hole-like charge carriers has been illustrated by Hall effect measurements. The general phase diagram looks very similar to that of the cuprate, implying a very fundamental constraint on the mechanisms of the two systems.

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Author Contributions: HHW designed and coordinated the whole experiment, including the details about the doping and the synthesizing, and did part experiments, analyzed the data and wrote the paper. GM, LF and XYZ equally contributed to the synthesizing and part of the magnetic measurements, LF did the structure analysis. HY did the resistive and Hall measurements.

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