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

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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\(_x\)CoO\(_2\)-1.3H\(_2\)O [3], Sr\(_2\)RuO\(_4\) [4], etc., but all these have the transition temperatures below 20 K. Searching new superconductors with 3\(_d\) or 4\(_d\) transition metal compounds is especially 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 oxy-pnictides 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 \(P4/\text{mm}m\) space group, with a stacking series of \((\text{LnO})_2-(\text{MP})_2-(\text{LnO})_2-\). In one unit cell, there are two molecules of LnOMP, and it is valence self-balanced, \(\text{i.e.,} (\text{LaO})^{+1}\) is balanced by \((\text{MP})^{-1}\). Some of them, such as LaOF\(_e\)P and LaONiP, were shown to be superconductors at about 4 K [6] and 3 K [7], respectively. By substituting the oxygen with F, \(T_c\) was increased to 7K [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 O in LaOFeP with F, the resultant material La(O\(_{1-x}\)F\(_x\))FeAs \((x = 0.05–0.12)\) 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 the experimental and the 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.

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The EDX spectrum taken from one of the main grains, which show 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.

Sample preparation and experiment. – By using a two-step method, we successfully fabricated the \((\text{La}_{0.87}\text{Sr}_{0.13})\text{OFeAs}\) \((x = 0.10–0.30)\) and \(\text{La}(\text{O}_{0.9}\text{F}_{0.1–\delta})\text{FeAs}\) \([13]\) samples. First the starting materials Fe powder (purity 99.95%) and As grains (purity 99.99%) were ground 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 ground together with the \(\text{SrCO}_3\) powder (purity 99.9%), \(\text{La}_2\text{O}_3\) powder (purity 99.9%) and grains of La (purity 99.99%) in stoichiometry as the formula \((\text{La}_{1–x}\text{Sr}_x)\text{OFeAs}\). Again it was pressed into a pellet and sealed in an evacuated quartz tube and burned at about 940 °C for 4 hours, followed by a burning at 1150 °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 \((\text{La}_{0.87}\text{Sr}_{0.13})\text{OFeAs}\). 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 also appear. Beyond that doping, some strong peaks from still impurity phase emerge and get stronger with more doping. But the XRD taken from all samples gives clear evidence that the main peaks are from the phase \((\text{La}_{1–x}\text{Sr}_x)\text{OFeAs}\). From fig. 1(a), it is clear that almost all main peaks can be indexed by a tetragonal structure with \(a = b = 4.0350 \text{Å}\) and \(c = 8.7710 \text{Å}\). These lattice constants are a bit larger than those in the parent phase \(\text{LaOFeAs}\) \((a = b = 4.032 \text{Å}\) and \(c = 8.726 \text{Å}\)), suggesting that the lattice expands a bit with Sr substitution, especially along the \(c\)-axis. This is understandable since the radius of \(\text{Sr}^{2+}\) is 1.12 Å which is larger than that of \(\text{La}^{3+}(1.06 \text{Å})\). Therefore, it is certain that the dominant component is from \((\text{La}_{0.87}\text{Sr}_{0.13})\text{OFeAs}\). 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 \((\text{La}_{1–x}\text{Sr}_x)\text{OFeAs}\).

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 was 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.

Results and discussion. – In fig. 2(a) we present the temperature dependence of the resistive transitions for samples \((\text{La}_{1–x}\text{Sr}_x)\text{OFeAs}\) with \(x = 0.10–0.20\). One can see that the onset transition temperature taken with a criterion of 95% \(\rho_n\) shifts slowly to higher values with the doping amount of Sr from 0.10 to 0.13. The maximum onset \(T_c \approx 25.6 \text{K}\) is achieved at a doping of \(x = 0.13\) and the zero resistance temperature is about 15 K. Then the 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 \(\text{La}(\text{O}_{1–x}\text{F}_x)\text{FeAs}\) where \(T_c\) is rather stable in the middle doping regime \(x = 0.05–0.11\). 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 \(T_c\) vs. doping may be
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![Graph of resistivity vs temperature for different Sr concentrations](image)

*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 $T_c \approx 25.6$ K at the doping of 0.13. Beyond $x = 0.20$, no superconductivity was observed.*

...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 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 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 diamagnetization 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 allows 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% $\rho_n$. 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 do not 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 $\rho_{xy}$ for both (La$_{0.87}$Sr$_{0.13}$)OFeAs and the electron-doped sample La(0.9Fe$_{0.1}$)FeAs. It is clear that $\rho_{xy}$ is positive at all temperatures below 200 K for (La$_{0.87}$Sr$_{0.13}$)OFeAs leading to a positive Hall coefficient $R_H = \rho_{xy}/H$. This is in sharp contrast with the data of the electron-doped sample La(0.9Fe$_{0.1}$)FeAs [13]. The positive Hall resistivity appears for all Sr-doped samples. In fig. 4(b) the temperature-dependent Hall coefficients of the two samples are shown. One can see that the Hall...
Fig. 4: Hall effect measurements for one sample (La$_{0.87}$Sr$_{0.13}$)OFeAs in the present work and an electron-doped sample La(O$_{0.9}$F$_{0.1}$)FeAs. (a) Magnetic-field dependence of Hall resistivity $\rho_{xy}$ 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 a 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 a wide temperature region. But a much stronger temperature dependence was observed which may suggest a multiband effect in the hole-doped samples.

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

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 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 a 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 obtain $n$ (electron doped) = $9.8 \times 10^{20}$/cm$^3$, while $n$ (hole doped) = $4.57 \times 10^{20}$/cm$^3$, both have a low 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 the 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 do not 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 the 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 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 play 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 a 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 trivalent element La partially by the 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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