Synthesizing and characterization of hole doped nickel based superconductor 
(La$_{1-x}$Sr$_x$)NiAsO

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We report the synthesizing and characterization of the hole doped Ni-based superconductor (La$_{1-x}$Sr$_x$)NiAsO. By substituting La with Sr, the superconducting transition temperature $T_c$ is increased from 2.4 K of the parent phase LaNiAsO to 3.7 K at the doping levels $x = 0.1$ - 0.2. The curve $T_c$ versus hole concentration shows a symmetric behavior as the electron doped samples LaNiAs(O$_{1-x}$F$_x$). The normal state resistivity in Ni-based samples shows a good metallic behavior and reveals the absence of spin density wave induced anomaly which appears in the Fe-based system at about 150 K. Hall effect measurements indicate that the electron conduction in the parent phase LaNiAsO is dominated by electron-like charge carriers, while with more Sr doping, a hole-like band will emerge and finally prevail over the conduction, such a phenomenon reflects that the Fermi surface of LaNiAsO comprises of electron pockets and hole pockets, thus the sign of charge carriers could be changed once the contribution of hole pockets overwhelms that of electron pockets. Magneto-resistance measurements and the violation of Kohler rule provide further proof that multiband effect dominate the normal state transport of (La$_{1-x}$Sr$_x$)NiAsO.

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Searching for high temperature superconductors has been a long-term strategy in material science. Superconductors with unconventional pairing symmetry found in past decades seem to have some common features: layered structure, such as in cuprates[1]; tunable transition temperature ($T_c$) by doping holes or electrons; possible exotic pairing mechanism rather than phonon mediated superconductivity, for instance in the heavy fermion system[2]. The newly discovered iron-based superconductor LaFeAs(O$_{1-x}$F$_x$) with a moderate high $T_c = 26$ K seems to fit to these three categories[3]. It is found that LaFeAs(O$_{1-x}$F$_x$) belongs to a layered structure constructed by stacking the LaO and FeAs sheets alternatively, where FeAs sheet is regarded as the conduction layer whose charge carrier density could be tuned by the neighboring LaO sheet by charge doping. Substituting part of the oxygen with fluorine, the system changes from having a weak insulating behavior to superconductive with $x = 0.05$ - 0.12[4]. This discovery has stimulated intense efforts in both experimental and theoretical studies. Theoretically it was concluded that the electronic correlation of this system could be moderate[7]. Experimentally both low temperature specific heat[5] and point contact tunneling[6] measurements indicate the possible unconventional pairing symmetry. LnFeAsO$_{1-x}$F$_x$ (Ln represents the rare earth element La, Ce, Pr, Nd, Sm, Gd) has been proved to be bearing electron type carriers, thus the possibility to realize hole doped superconductor in such a system is very attractive. The first stride has been successfully made in hole doped samples (La$_{1-x}$Sr$_x$)FeAsO with $T_c = 25$K by our group[9]. More recently hole doped La$_{1-x}$Ca$_x$FePO and (Ba$_{1-x}$K$_x$)Fe$_2$As$_2$ have been reported to realize superconductivity[13, 14]. In present work we report the fabrication and characterization of the hole doped Ni-based superconductors (La$_{1-x}$Sr$_x$)NiAsO. Superconductivity at about 3.7 K was found and the $T_c$ exhibits a symmetric behavior in both hole-doped and electron-doped side. The hole-like charge carriers in the present Sr doped sample (high doping) are evidenced by Hall effect measurements.

Polycrystalline (La$_{1-x}$Sr$_x$)NiAsO samples ( $x = 0.1$, 0.2, 0.3) were synthesized by the conventional solid state reaction method. Stoichiometric LaAs powder was home made by reacting pure La (99.99%) and As (99.99%). Later it is mixed with dehydrated La$_2$O$_3$ (99.9%), SrO...
(99.5%), and NiAs powder (home made by reacting pure Ni (99.99%) and As (99.99%), and Ni powder (99.99%), grounded and pressed into a pellet. Then the pellet was sealed into an evacuated quartz tube. Consequently, the tube was slowly warmed up in a muffle furnace to 1150 °C and sintered for 48 hours, then cooled down to room temperature. X-ray diffraction (XRD) pattern measurement was performed at room temperature employing an M18AHF x-ray diffractometer (MAC Science). The magnetic measurements were carried out on a Magnetic Property Measurement System (MPMS, Quantum Design). The electrical resistivity and Hall coefficient were measured by a six-probe method based on a Physical Property Measurement System (PPMS, Quantum Design).

Fig. 1 presents the schematic illustration of (La$_{1-x}$Sr$_x$)NiAsO structure. Parts of La$_3^+$ coordinations were occupied by Sr$_{2^+}$. Fig. 2 shows the XRD pattern of the sample (La$_0.8$Sr$_{0.1}$)NiAsO, which can be indexed in a tetragonal space group with $a = b = 4.1290$ Å and $c = 8.1936$ Å. Though minor peaks arising from the impurity phase were found (could come from NiAs), there is no doubt that the main phase is dominated by (La$_{1-x}$Sr$_x$)NiAsO in the sample with $x = 0.1$. Crystalline quality of (La$_0.8$Sr$_{0.2}$)NiAsO is similar to that of 0.1 doping but with a bigger lattice parameter ($a = b = 4.1483$ Å and $c = 8.2105$ Å). Comparing to the indices of parent phase LaNiAsO ($a = b = 4.12309$ Å and $c = 8.18848$ Å), cell parameters of strontium doped (La$_{1-x}$Sr$_x$)NiAsO are a bit larger. As to the 0.3 doping, it is observed that lots of impurity peaks dominated the XRD pattern, indicating stronger phase segregation during the sintering. Taking account of the sandwich structure of LaNiAsO, structure distortion of LaO sheet caused by incommensurate replacement of La$_3^+$ by Sr$_{2^+}$ is restricted by the neighboring NiAs sheets, thus it is believed that the quantity of chemical doping is limited on certain extent. Therefore in the following discussion, the data of (La$_0.7$Sr$_{0.3}$)NiAsO are not included. An interesting result is that the cell parameters increase with the Sr doping, meanwhile $T_c$ also increases and saturates to high doping (shown in the following section). However, electron doped (fluorine) and hole doped (calcium) materials have shown that $T_c$ is proportional to the shrinkage of cell parameters

$$c = 8.18848 \text{ Å}$$

It should be pointed that La$_3^+$ and Sr$_{2^+}$ ions have radius of 1.06 Å and 1.12 Å, respectively. The size difference is not that big. Thus we suggest that for hole doped LaNiAsO chemical pressure could not be the only parameter to influence $T_c$, the band filling may also play an important role.

The DC magnetization data of (La$_{1-x}$Sr$_x$)NiAsO were shown in Fig. 3(a). Fig. 3(b) shows the temperature dependence of resistivity under different magnetic fields. A

![FIG. 2: (Color online) XRD pattern of (La$_{1-x}$Sr$_x$)NiAsO with $x = 0.1$, which can be indexed in a tetragonal symmetry with $a = b = 4.1290$ Å and $c = 8.1936$ Å. The asterisks mark the peaks from impurity phase.](image)

![FIG. 3: (Color online) (a) DC magnetization of (La$_{1-x}$Sr$_x$)NiAsO samples with $x = 0.1$ and 0.2, measured in the zero-field-cooled (ZFC) and field-cooled (FC) processes. The superconducting fraction estimated at 2 K is beyond 40 %. (b) The temperature dependence of resistivity of the sample with $x = 0.1$ under different magnetic fields.](image)
sharp transition with the width of about 0.4 K is observed at 3.7 K. By applying a magnetic field, the resistive transition curve broadens quickly showing a strong vortex flow behavior. But the onset transition point, which is close to the upper critical field, moves slowly with the magnetic field. This is similar to that observed in F-doped \( \text{LaFeAsO} \) \[10\]. Compared with the pure phase \( \text{LaNiAsO} \) with \( T_c \approx 2.4 \) K \[15\], \( T_c \) of strontium substituted samples are improved to 3.7 K and 3.5 K for doping \( x=0.1 \) and 0.2, respectively. According to Ginzburg-Landau theory, zero temperature upper critical field \( H_{c2}(0) \) could be derived from the formula:

\[
H_{c2}(T) = H_{c2}(0)(1-t^2)/(1+t^2),
\]

where \( t \) is the normalized temperature \( T/T_c \). It is found that the theoretical curve can fit the experimental data very well. The derived \( H_{c2}(0) \) is found to be about 5.5 T, being close to that in the F-doped Ni-based system \[11\].

Fig.4(a) shows the resistivity of \( (\text{La}_{0.8}\text{Sr}_{0.2})\text{NiAsO} \) with \( x = 0.1, 0.2 \) from 2 K to 300 K at zero field. The resistivity in the normal state for all doping levels show metallic behavior. Near 3.7 K the resistivity of \( (\text{La}_{0.9}\text{Sr}_{0.1})\text{NiAsO} \) drops sharply to zero, whereas, the resistivity of \( (\text{La}_{0.8}\text{Sr}_{0.2})\text{NiAsO} \) drops at about 3.5 K with a similar transition width. For a better comparison, the resistivity of \( \text{LaNiAsOs}(0.0,9)\text{F}_{0.1} \) with \( T_c \approx 3.8 \) K was also shown in Fig.4(a). It is interesting to note that, at all doping levels the normal state resistivity of the present Ni-based system exhibit no anomaly as found in the F-doped Fe-based system at about 150 K \[12\]. A possible explanation is that there is a big difference in spin moment between Fe ion and Ni ion \[10\].

In Fig.4(b) we show an enlarged view for the resistive transitions for samples with \( x=0.1 \) and 0.2. The transition temperature of sample \( x=0.2 \) is about 3.5 K, which is very close to that of sample \( x=0.1 \), but obviously higher than that of the undoped parent phase \( \text{LaNiAsO} \) \( (T_c \approx 2.4 K) \). Interestingly, if we plot the \( T_c \) versus the hole concentration, the curve exhibits a symmetric behavior with the electron doped side \[11\]. This behavior has also been found in our original work for hole doped \( (\text{La}_{1-x}\text{Sr}_{x})\text{FeAsO} \) system. The similar behavior in both systems may suggest that the density of states in the two sides of the Fermi energy is roughly symmetric. Band structure calculation based on generalized gradient approximation (GGA) functional has revealed that density of state is roughly particle-hole symmetric in antiferromagnetic \( \text{LaFeAsO} \) \[17\]. As to \( \text{LaNiAsO} \), also, band calculation using GGA gave a similar result \[18\].

Since part of \( \text{La}^{3+} \) are substituted by \( \text{Sr}^{2+} \), hole typed carriers are expected in our present \( \text{Sr} \)-doped system. A prove to that by Hall effect measurements is necessary. Fig.5(a) and Fig.5(b) show the Hall resistivity \( \rho_{xy} \) for sample \( x = 0.1 \) and 0.2, respectively. Interestingly, the sign of \( \rho_{xy} \) for \( x = 0.1 \) is still negative, but quite close to zero. This is reasonable since the parent phase \( \text{LaNiAsO} \) is actually dominated by an electron-like band \[11\], the Hall coefficient defined as \( R_H = \rho_{xy}/H \) is \(-5 \times 10^{-10} \text{m}^2/\text{C} \) at 100 K for the undoped sample. This means that holes are really introduced into the system by doping \( \text{Sr} \). By doping more \( \text{Sr} \) into the system, the Hall resistivity \( \rho_{xy} \) becomes positive and hole-like charge carriers finally dominate the conduction at the doping level \( x = 0.2 \). Fig.6 presents the Hall coefficient for two samples below 100 K. It is clear that \( (\text{La}_{0.9}\text{Sr}_{0.1})\text{NiAsO} \) has more electron-like charge carriers, but the sample \( (\text{La}_{0.8}\text{Sr}_{0.2})\text{NiAsO} \) shows clearly the dominant conduction by hole-like charge carriers. Our data suggest that with the substitution of \( \text{La}^{3+} \) by \( \text{Sr}^{2+} \), the conduction by the electron-like band which appears for the undoped phase will be prevailed over by the hole-like band, and superconductivity at about 3.5-3.8 K occurs when the hole-like band dominates the conduction. Moreover, such a phenomenon reflects that the Fermi surface of \( \text{LaNiAsO} \) does comprise of electron pockets and hole pockets, thus the sign of charge carriers could be changed once the contribution of hole pockets overwhelms that of electron
pockets.

Changing sign of Hall coefficient reveals the possible multiband effect in the normal state of $(La_{1-x}Sr_x)NiAsO$, thus magnetoresistance (MR) measurements and the suitability of Kohler’s rule is worth investigating. Fig.7(a) shows the magnetoresistance versus the magnetic field at different temperatures. It is found that the MR is about 2.7% at 4K and 9T. Fig.7(b) shows the scaling to the Kohler’s rule, obviously the Kohler rule is violated. It is believed that Kohler’s law is conserved on single band metal with symmetric Fermi surface topology. Therefore the magnetoresistance effect and violation of Kohler’s rule reveal that multiple bands cross the Fermi surface. However taking account of the polycrystalline samples that our experiments based on, we could not exclude the skew scattering process caused by minor magnetic impurities, thus single crystal samples of LaONiAs is strongly desired.

In summary, by substituting La with Sr in $LaNiAsO$, a systematic change of both the superconducting transition temperature and normal state Hall coefficient are observed. First the transition temperature is increased from 2.4 K to about 3.5 - 3.8 K with Sr doping, meanwhile the Hall coefficient changes from negative to positive. The curve of $T_c$ vs. the hole concentration exhibits a symmetric behavior as the electron doped side, which may suggest a roughly symmetric distribution of DOS above and below the Fermi energy. Our data further support the conclusion that superconductivity can be induced by hole doping.

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FIG. 5: (Color online) Hall resistivity as a function of applied magnetic field for samples $(La_{1-x}Sr_x)NiAsO$, $x = 0.1$ (a) and 0.2 (b), respectively. The Hall resistivity is small in magnitude compared with the electron doped or undoped samples, indicating the gradual emergence of a hole-like conduction band.

FIG. 6: (Color online) Hall coefficients for samples $(La_{1-x}Sr_x)NiAsO$ with $x = 0.1$ and 0.2. A sign change is obvious with increasing Sr content from 0.1 to 0.2 indicating a dominant conduction by hole-like charge carriers at $x = 0.2$.

FIG. 7: (Color online) (a) Field dependence of magnetoresistance $\Delta \rho / \rho_0$ at different temperatures for sample $(La_{0.9}Sr_{0.1})NiAsO$. (b) Kohler plot at different temperatures, and obviously the Kohler rule is violated.
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