Synthesis and characterization of the hole-doped nickel-based superconductor $La_{1-x}Sr_xNiAsO$

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We report the synthesizing and characterization of the hole-doped Ni-based superconductor $La_{1-x}Sr_xNiAsO$. 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 a 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 electronlike charge carriers, while with more Sr doping, a holelike band will emerge and finally prevail over the conduction. Such a phenomenon reflects that the Fermi surface of LaNiAsO comprises of electron and hole pockets; thus the sign of charge carriers could be changed once the contribution of hole pockets overwhelms that of electron pockets. Magnetoresistance measurements and the violation of the Kohler rule provide further proof that multiband effect dominates the normal-state transport of $La_{1-x}Sr_xNiAsO$.

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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; and possible exotic pairing mechanism rather than phonon mediated superconductivity, for instance in the heavy fermion system.[2] The recently 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.[3–6] 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.[7,8] 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 elements La, Ce, Pr, Nd, Sm, and Gd) has been proved to be bearing electron-type carriers; thus the possibility of realizing a hole-doped superconductor in such a system is very attractive. The stride has been successfully made in hole-doped samples $La_{1-x}Sr_xFeAsO$ with $T_c=25$ K by our group.[9] More recently hole-doped $La_{1-x}Ca_xFePO$ and $(Ba_{1-x}K_x)Fe_2As_2$ have been reported to realize superconductivity.[10,11] In present work we report the fabrication and characterization of the hole-doped Ni-based superconductors $La_{1-x}Sr_xNiAsO$. Superconductivity at about 3.7 K was found, and the T_c exhibits a symmetric behavior in both hole-doped and electron-doped sides. The holelike charge carriers in the present Sr-doped sample (high doping) are evidenced by Hall-effect measurements.

Polycrystalline $La_{1-x}Sr_xNiAsO$ samples ($x=0.1$, 0.2, and 0.3) were synthesized by the conventional solid-state reaction method. Stoichiometric LaAs powder was homemade by reacting pure La (99.99%) and As (99.99%). Later it was mixed with dehydrated La_2O_3 (99.9%), SrO (99.5%), NiAs powder [homemade 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 h, 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).

Figure 1 presents the schematic illustration of the $La_{1-x}Sr_xNiAsO$ structure. Parts of La^{3+} coordinations were occupied by Sr^{2+}. Figure 2 shows the XRD pattern of the sample $La_{0.9}Sr_{0.1}NiAsO$, which can be indexed in a tetragonal space group with $a=b=4.1290$ Å and $c=8.1936$ Å.

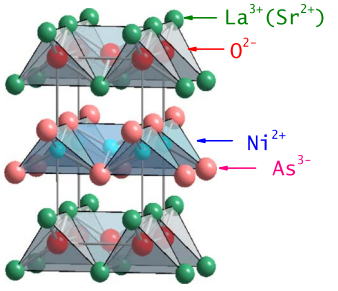

FIG. 1. (Color online) Schematic illustration of $La_{1-x}Sr_xNiAsO$ structure. Parts of La^{3+} coordinations were occupied by Sr^{2+}, thus hole was implanted into parent phase LaNiAsO.

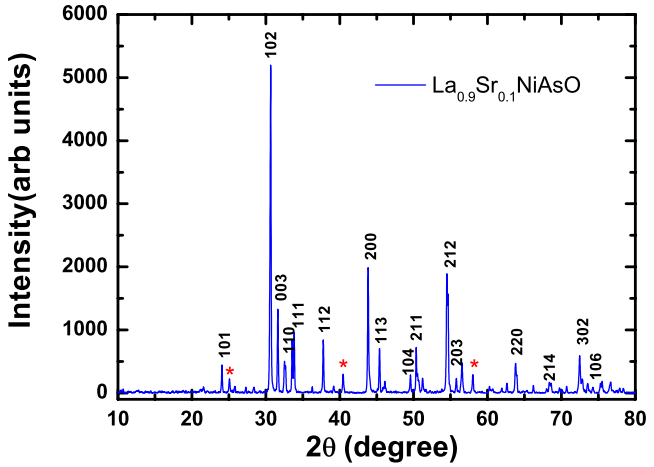

FIG. 2. (Color online) XRD pattern of $La_{1-x}Sr_xNiAsO$ with $x=0.1$, which can be indexed in a tetragonal symmetry with $a=b=4.1290$ Å and $c=8.1936$ Å. The asterisks mark the peaks from impurity phase.

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 $La_{1-x}Sr_xNiAsO$ in the sample with $x=0.10$. 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),[12] cell parameters of strontium doped $La_{1-x}Sr_xNiAsO$ 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 the 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 to a 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.[10] It should be pointed that La^{3+} and Sr^{2+} ions have radius of 1.06 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 $La_{1-x}Sr_xNiAsO$ were shown in Fig. 3(a). Figure 3(b) shows the temperature dependence of resistivity under different magnetic fields. A 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 LaFeAsO.[13] Compared with the pure phase LaNiAsO with $T_c \approx 2.4$ K,[12] T_c of strontium substituted samples are improved to 3.7 and 3.5 K for doping

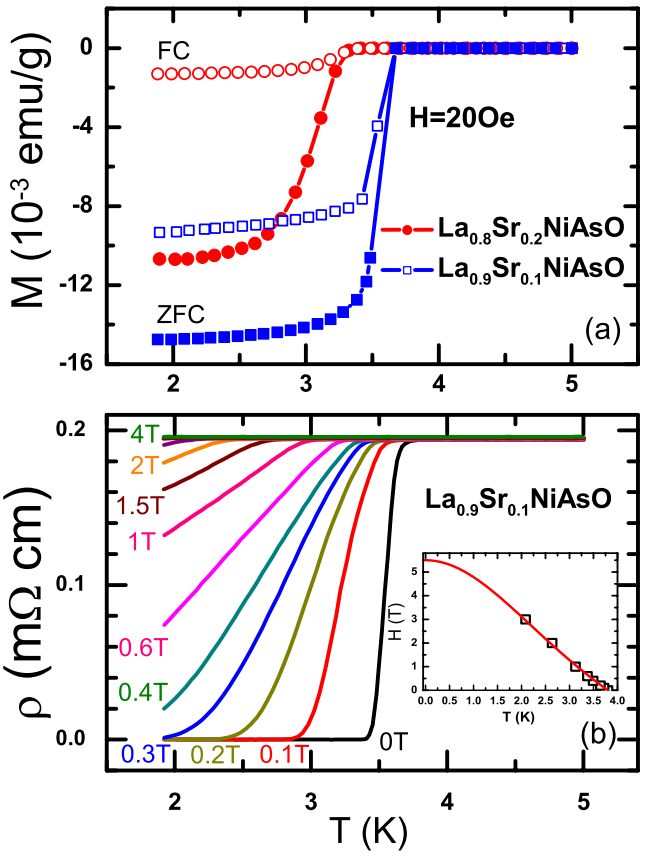

FIG. 3. (Color online) (a) dc magnetization of $La_{1-x}Sr_xNiAsO$ samples with $x=0.1$ and 0.2 measured in the zero-field cooled (ZFC) and field cooled (FC) processes. The superconducting fraction estimated at 2 K is beyond 40%. (b) The temperature dependence of resistivity of the sample with $x=0.1$ under different magnetic fields. It is clear that the superconducting transition is broadened by using a magnetic field. The upper critical field is determined with the criterion $\rho=95\%\rho_n$ and shown as an inset of Fig. 2(b). The solid line in the inset shows the theoretical fitting based on the GL theory (see text).

$x=0.1$ and 0.2, respectively. According to Ginzburg-Landau (GL) 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.[14]

Figure 4(a) shows the resistivity of $La_{1-x}Sr_xNiAsO$ with $x=0.1$ and 0.2 from 2 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 $La_{0.9}Sr_{0.1}NiAsO$ drops sharply to zero, whereas the resistivity of $La_{0.8}Sr_{0.2}NiAsO$ drops at about 3.5 K with a similar transition width. For a better comparison, the resistivity of $LaNiAs(O_{0.9}F_{0.1})$ 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.[15] A possible explanation is that there is a big difference in spin moment between Fe and Ni ions.[16]

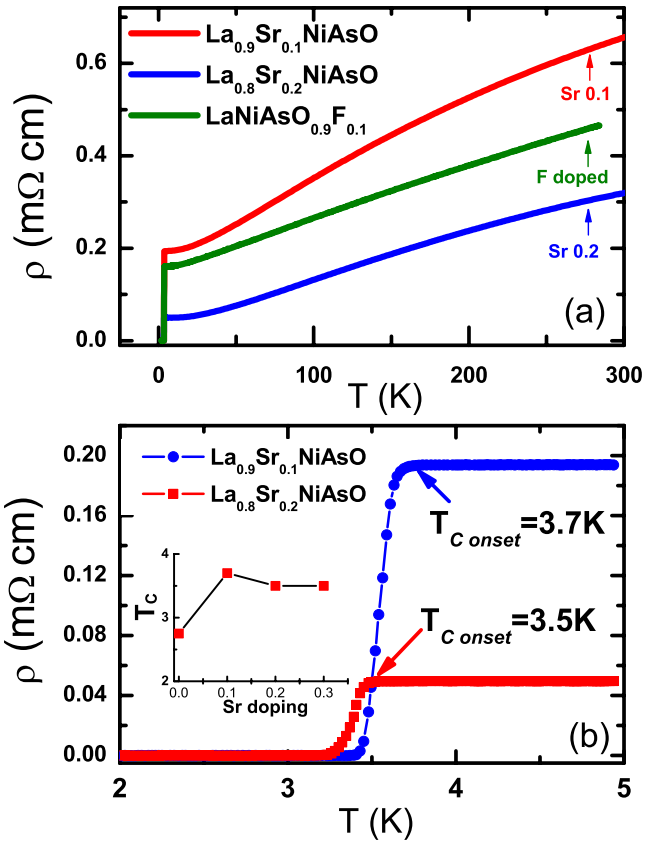

FIG. 4. (Color online) (a) Temperature dependence of resistivity in wide temperature region for samples with $x=0.1$ and 0.2, and the electron-doped sample $LaNiAs(O_{0.9}F_{0.1})$. The normal state does not exhibit an anomaly, which appears in the Fe-based system. (b) An enlarged view for the resistive transitions of the samples with $x=0.1$ and 0.2. The inset in Fig. 3(b) presents the hole doping dependence of the transition temperature. Combining the data from the electron-doped side, it is found that the curve of T_c vs hole and electron concentrations exhibits a symmetric behavior.

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 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.[14] This behavior has also been found in our original work for the hole-doped $La_{1-x}Sr_xFeAsO$ system. The similar behavior in both systems may suggest that the density of states (DOS) in the two sides of the Fermi energy is roughly symmetric. Band-structure calculation based on the generalized gradient approximation (GGA) functional has revealed that density of state is roughly particle-hole symmetric in antiferromagnetic LaFeAsO.[17] As to LaNiAsO, also, band calculation using GGA gave a similar result.[18]

Since part of La^{3+} are substituted by Sr^{2+}, hole-typed carriers are expected in our present Sr-doped system. A proof to that by Hall-effect measurements is necessary. Figures 5(a) and 5(b) show the Hall resistivity ρ_{xy} for sample $x=0.1$ and 0.2, respectively. Interestingly, the sign of ρ_{xy} for $x=0.1$ is still negative but quite close to zero. This is reasonable since

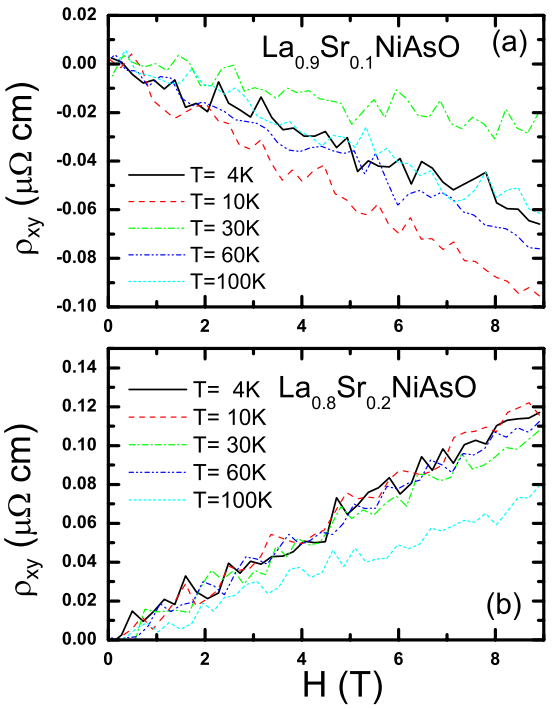

FIG. 5. (Color online) Hall resistivity as a function of applied magnetic field for samples $La_{1-x}Sr_xNiAsO$, (a) $x=0.1$ and (b) 0.2, respectively. The Hall resistivity is small in magnitude compared with the electron-doped or undoped samples indicating the gradual emergence of a holelike conduction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

the parent phase LaNiAsO is actually dominated by an electronlike band,[14] the Hall coefficient defined as $R_H=\rho_{xy}/H$ is -5×10^{-10} m^3/C at 100 K for the undoped sample. This means that holes are really introduced into the system by doping Sr. By doping more Sr into the system, the Hall resistivity ρ_{xy} becomes positive and holelike charge carriers finally dominate the conduction at the doping level $x=0.2$. Figure 6 presents the Hall coefficient for two samples below 100 K. It is clear that $La_{0.9}Sr_{0.1}NiAsO$ has more electronlike charge carriers, but the sample $La_{0.8}Sr_{0.2}NiAsO$ shows clearly the dominant conduction by holelike charge carriers. Our data suggest that with the substitution of La^{3+} by Sr^{2+},

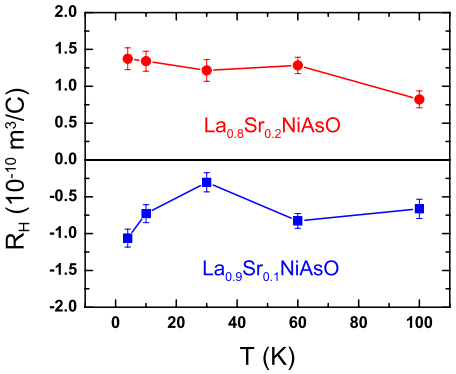

FIG. 6. (Color online) Hall coefficients for samples $La_{1-x}Sr_xNiAsO$ with $x=0.1$ and 0.2. A sign change is obvious with increasing Sr content from 0.1 to 0.2 indicating a dominant conduction by holelike charge carriers at $x=0.2$.

the conduction by the electronlike band, which appears for the undoped phase, will be prevailed over by the holelike band, and superconductivity at about 3.5–3.8 K occurs when the holelike band dominates the conduction. Moreover, such a phenomenon reflects that the Fermi surface of LaNiAsO does comprise electron and hole pockets; thus the sign of charge carriers could be changed once the contribution of hole pockets overwhelms that of electron pockets.

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

In summary, by substituting La with Sr in LaNiAsO, a systematic change in 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.

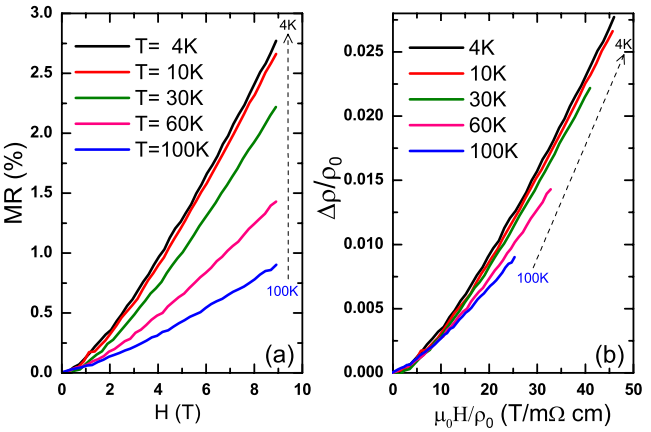

FIG. 7. (Color online) (a) Field dependence of magnetoresistance $\Delta\rho/\rho_0$ at different temperatures for sample $La_{0.9}Sr_{0.1}NiAsO$. (b) Kohler plot at different temperatures, and obviously the Kohler rule is violated.

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