Synthesis, structural and transport properties of the hole-doped Superconductor

Pr$_{1-x}$Sr$_x$FeAsO

Gang Mu, Bin Zeng, Xiyu Zhu, Fei Han, Peng Cheng, Bing Shen, and Hai-Hu Wen

National Laboratory for Superconductivity, Institute of Physics and Beijing National Laboratory for Condensed Matter Physics, Chinese Academy of Sciences, P. O. Box 603, Beijing 100190, People’s Republic of China

Superconductivity was achieved in PrFeAsO by partially substituting Pr$^{3+}$ with Sr$^{2+}$. The electrical transport properties and structure of this new superconductor Pr$_{1-x}$Sr$_x$FeAsO at different doping levels ($x = 0.05$ ~$0.25$) were investigated systematically. It was found that the lattice constants ($a$-axis and $c$-axis) increase monotonously with Sr or hole concentration. The superconducting transition temperature at about 16.3 K ($95\%\rho_0$) was observed around the doping level of 0.20~0.25. A detailed investigation was carried out in the sample with doping level of $x = 0.25$. The domination of hole-like charge carriers in this material was confirmed by Hall effect measurements. The magnetoresistance (MR) behavior can be well described by a simple two-band model. The upper critical field of the sample with $T_c = 16.3$ K ($x = 0.25$) was estimated to be beyond 45 Tesla. Our results suggest that the hole-doped samples may have higher upper critical fields comparing to the electron-doped ones, due to the higher quasi-particle density of states at the Fermi level.

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I. INTRODUCTION

The discovery of superconductivity at 26 K in FeAs-based layered quaternary compound LaFeAsO$_{1-x}$F$_x$ has attracted great interests in the fields of condensed matter physics and material sciences. The family of the FeAs-based superconductors has been extended rapidly and it can be divided into three categories. The first category has the general formula of REFeAsO where RE stands for the rare earth elements and is abbreviated as the FeAs-1111 phase. The second class is formulated as (Ba, Sr)$_{1-x}$K$_x$Fe$_2$As$_2$ which is denoted as FeAs-122 for simplicity. The third type Li$_x$FeAs has an infinite layered structure (denoted as FeAs- 1111). As for the FeAs-1111 phase, most of the discovered superconductors are characterized as electron doped ones and the superconducting transition temperature has been quickly raised to $T_c = 55$~66 K via replacing lanthanum with other rare earth elements. About the hole-doped side, however, since the first hole-doped superconductor La$_{1-x}$Sr$_x$FeAsO with $T_c \approx 25$ K was discovered only the Nd-based system Nd$_{1-x}$Sr$_x$FeAsO with $T_c = 13.5$ K was reported. Obviously, there is an extensive space to explore more superconductors in the hole-doped side based on the FeAs-1111 phase and to further extend the family of the FeAs-based superconductors. And it is also significant to investigate the basic physical properties of the hole-doped system based on the FeAs-1111 phase.

In this paper we report a new route to easily synthesize the hole-doped superconductors based on the FeAs-1111 phase, Sr doped Pr$_{1-x}$Sr$_x$FeAsO, with the maximum superconducting transition temperature of 16.3 K. We carried out a systematic study on the evolution of the superconductivity and the lattice constants with the content of Sr or hole concentration in the system of Pr$_{1-x}$Sr$_x$FeAsO. We found that the $a$-axis and $c$-axis lattice constants increase monotonously with doped concentration of Sr or hole numbers. The physical properties of a selected sample with $x = 0.25$ were investigated in depth. The conducting charge carriers in this sample were characterized to be hole type by the Hall effect measurements. And it is found that the MR data show a good two-band behavior. We also estimated the upper critical field of the same sample based on the Ginzburg-Landau theory as well as the Werthamer-Helfand-Hohenberg (WHH) formula. It is suggested that the upper critical fields in the hole-doped samples may be higher than that in the electron-doped ones.

II. EXPERIMENTAL DETAILS

The Pr$_{1-x}$Sr$_x$FeAsO samples were prepared using a two-step solid state reaction method. In the first step, PrAs and SrAs were prepared by reacting Pr flakes (purity 99.999%), Sr flakes (purity 99.9%) and As grains (purity 99.99%) at 500 °C for 8 hours and then 700 °C for 16 hours. They were sealed in an evacuated quartz tube when reacting. Then the resultant precursors were thoroughly grounded together with Fe powder (purity 99.95%) and Fe$_2$O$_3$ powder (purity 99.5%) in stoichiometry as given by the formula Pr$_{1-x}$Sr$_x$FeAsO. All the weighing and mixing procedures were performed in a glove box with a protective argon atmosphere. Then the mixtures were pressed into pellets and sealed in a quartz tube with an atmosphere of 20% Ar. The materials were heated up to 1150 °C with a rate of 120 °C/hr and maintained for 60 hours. Then a cooling procedure was followed. It is important to note that the use of SrAs as the starting material, instead of using SrCO$_3$ or SrO, is very essential to synthesize the high quality samples, and to much suppress the secondary impurity phases. This new route makes our hole-doped samples easily reproduced.

The X-ray diffraction (XRD) measurements of our...
samples were carried out by a Mac-Science MXP18A-HF equipment with θ-2θ scan. The dc magnetization measurements were done with a superconducting quantum interference device (Quantum Design, SQUID, MPMS7) and the ac susceptibility of the samples was measured on the Maglab-12T (Oxford) with an ac field of 0.1 Oe and a frequency of 333 Hz. The resistance and Hall effect measurements were done using a six-probe technique on the Quantum Design instrument physical property measurement system (PPMS) with magnetic fields up to 9 T. The temperature stabilization was better than 0.1% and the resolution of the voltmeter was better than 10 nV.

III. EXPERIMENTAL DATA AND DISCUSSION

A. Resistive and diamagnetic transition

In Fig.1 (a) we present a typical set of resistive data for the sample Pr$_{1-x}$Sr$_x$FeAsO with $x = 0.25$ under 0 T and 9 T near the superconducting transition. One can see that the resistivity transition at zero field is rather sharp indicating the quite high quality of our sample, and the onset transition temperature is about 16.3 K taking a criterion of 95% $ρ_n$. A magnetic field of 9 T only depresses the onset transition temperature about 2.5 K but makes the superconducting transition broader. The former behavior may indicate a rather high critical field in our sample, while the latter reflected the weak link between the grains.\textsuperscript{19} Fig.1 (b) shows the zero field cooled and also the field cooled dc magnetization of the same sample at 10 Oe. And the diamagnetic transition measured with ac susceptibility technique is shown in the inset of Fig.1 (b). A rough estimate from the diamagnetic signal shows that the superconducting volume fraction of the present sample is beyond 50%, confirming the bulk superconductivity in our samples. The onset critical temperature by magnetic measurements is roughly corresponding to the zero resistivity temperature.

Shown in Fig. 2 is the temperature dependence of resistivity under zero field up to 300 K for the same sample as shown in Fig. 1. The resistivity data in the normal state were fitted using the formula

$$ρ = ρ_0 + AT^n,$$

as we had done in the F-doped LaFeAsO system.\textsuperscript{19} As represented by the red solid line in Fig. 2, the data below about 150 K can be roughly fitted with the fitting parameters $ρ_0 = 0.306$ mΩ cm and $n = 2.000$. The fine quadratic dependent behavior of the resistivity, which is consistent with the prediction of the Fermi-liquid theory, may suggest a rather strong scattering between electrons in the present system in the low
B. Doping dependence of lattice constants and superconducting properties

The XRD patterns for the samples with the nominal doping levels of 0.05–0.25 are shown in Fig. 3. Some small peaks from small amount of FeAs impurity phase which were denoted by red asterisk can still be seen, and the sample with x = 0.05 has a bit more impurity phase FeAs than other samples. However, it is clear that all the main peaks can be indexed to the tetragonal ZrCuSiAs-type structure. By having a closer scrutiny one can find that the diffraction peaks shift slightly to the low-angle side, the variable "x" represents the fluorine concentration. The data of the undoped and F-doped cases (red filled circles) are taken from the work of Ren et al.\textsuperscript{13} One can see that the lattice constant roughly show a monotonous variation versus doping from electron doped region to hole-doped one.

FIG. 3: (Color online) X-ray diffraction patterns for Pr\textsubscript{1−x}Sr\textsubscript{x}FeAsO samples with different doping levels: x = 0.05, 0.10, 0.15, 0.20 and 0.25. One can see that all the main peaks can be indexed to the tetragonal ZrCuSiAs-type structure. Small amount of impurity phases were denoted by red asterisks.

FIG. 4: (Color online) Doping dependence of (a) a-axis lattice constant; (b) c-axis lattice constant. The black filled squares represent data from our measurements. For electron-doped side, the variable "x" represents the fluorine concentration. The data of the undoped and F-doped cases (red filled circles) are taken from the work of Ren et al.\textsuperscript{13}. We have pointed out that this behavior may be a common feature of the hole-doped FeAs-based superconductors\textsuperscript{16}.

Temperature region. In high temperature region above about 150 K, however, a flattening of resistivity was observed clearly. The similar behavior has been observed in other hole-doped FeAs-1111 systems La\textsubscript{1−x}Sr\textsubscript{x}FeAsO and Nd\textsubscript{1−x}Sr\textsubscript{x}FeAsO\textsuperscript{15,16,17} and also in the FeAs-122 system (Ba, Sr)\textsubscript{1−x}K\textsubscript{x}Fe\textsubscript{2}As\textsubscript{2}\textsuperscript{2}. We have pointed out that this behavior may be a common feature of the hole-doped FeAs-based superconductors\textsuperscript{16}.

that both the a-axis and c-axis lattice constants expand monotonously from 11\% F-doped PrFeAsO to the Sr-doped samples. This indicates that the strontium atoms go into the crystal lattice of the PrFeAsO system because the radii of Sr\textsuperscript{2+} (1.12 Å) is larger than that of Pr\textsuperscript{3+} (1.01 Å). It is worth noting that the extent of the lattice expanding is appreciably smaller than that in the Sr-doped LaFeAsO system, where the maximum onset transition temperature can be as high as 26 K\textsuperscript{15,16}. In some cases, we see a slight drop of resistivity at temperatures as high as 28 K. So we believe that a further increase in \( T_c \) is possible if more strontium can be chemically doped into this system, like in the case of Nd\textsubscript{1−x}Sr\textsubscript{x}FeAsO\textsuperscript{17}.

In Fig. 5 we show the resistivity data of our samples made at various nominal doping levels of Sr ranging from x = 0.05 to 0.25. A clear but rounded resistivity anomaly can be seen around 155–175 K when the doping level is 5\%. And a tiny resistivity drop at about 6 K which may be induced by the antiferromagnetic ordering of Pr\textsuperscript{3+} ions or superconductivity can be observed. At this time it is difficult to discriminate between the two scenarios since the magnitude of the resistivity drop is quite small. At the doping levels of 0.10–0.25, resis-
tivity anomaly in high temperature regime is suppressed gradually and it eventually evolves into a flattening behavior at high doping levels. Also the magnitude of resistivity reduces obviously compared with the sample with 5% doping, suggesting that more and more conducting carriers were introduced into the samples. At the same time, the superconductivity emerges with doping and becomes optimal with an onset transition temperature of 16.3 K when the doping level is x = 0.20~0.25. It is worth noting that the resistivity at high temperatures at a high doping level of holes behaves in a different way compared with that in the electron-doped samples.15,16,17,18,19,20 where the resistivity anomaly is suppressed completely and the resistivity always presents a metallic behavior in that regime. While in the hole-doped samples, the resistivity anomaly is smeared much slower.15,16,17 In the Nd1-xSrxFeAsO system,17 for example, it is found that the structural transition from tetragonal to orthorhombic occurs even in the sample with superconductivity. Doping more holes may lead to stronger suppression to the structural transition as well as the SDW order, this may leave a potential space to increase the superconducting transition temperature in the hole-doped FeAs-1111 phase.

### C. Hall effect

It is known that for a conventional metal with Fermi liquid feature, the Hall coefficient is almost independent of temperature. However, this situation is changed for a multiband material or a sample with non-Fermi liquid behavior, such as the cuprate superconductors.21 To get more information about the conducting carriers, we measured the Hall effect of the sample with x = 0.25 (the same one as shown in Fig. 1). Fig. 6(a) shows the magnetic field dependence of Hall resistivity (ρxy) at different temperatures. In the experiment ρxy was taken as ρxy = |ρ(+H) - ρ(-H)|/2 at each point to eliminate the effect of the misaligned Hall electrodes. It is clear that all curves in Fig. 6(a) have good linearity versus the magnetic field. Moreover, ρxy is positive at all temperatures below 250 K giving a positive Hall coefficient RH = ρxy/H, which actually indicates that hole type charge carriers dominate the conduction in the present sample.

The temperature dependence of RH is shown in Fig. 6(b). Very similar to that observed in La1-xSrxFeAsO samples,15,16 the Hall coefficient RH reveals a huge hump in the intermediate temperature regime and the value of RH decreases down to zero at about 250 K, then it becomes slightly negative above that temperature. Here we employ a simple two-band scenario with different types of carriers to interpret this behavior. We have known that for a two-band system in the low-field limit, the Hall co-
efficient $R_H$ can be written as

$$R_H = \frac{\sigma_1^2 R_1 + \sigma_2^2 R_2}{(\sigma_1 + \sigma_2)^2},$$  \hspace{1cm} (2)

where $\sigma_i$ ($i = 1, 2$) is the conductance for different types of charge carriers in different bands, and $R_i = -1/n_i e$ represents the Hall coefficient for each type of carriers separately with $n_i$ the concentration of the charge carriers for the different bands. We attribute the strong temperature dependence of $R_H$ in the present system to the complicated variation of the conductance $\sigma_i$ with temperature, which reflects mainly the temperature dependent behavior of the scattering relaxation time. And the sign-changing effect of $R_H$ may indicate the presence of two different types of charge carriers (electron and hole type) in the present system. The conductance $\sigma_i$ of electron-like and hole-like carriers may vary differently with temperature, and the electron-like carriers become dominant when the temperature is higher than about 250 K.

This simple two-band model is consistent with the MR data (will be addressed in the next section). However, if there are two types of carriers in two bands, we may expect $\rho_{xy}$ to be quadratic in magnetic field. The linear behavior in the $\rho_{xy} \sim H$ curve shown in Fig. 6(a) seems to be not agree with this scenario. So further measurements with higher magnetic fields are required.

### D. Magnetoresistance

Magnetoresistance is a very powerful tool to investigate the electronic scattering process and the information about the Fermi surface. Field dependence of MR, for the sample with $x = 0.25$ at different temperatures is shown in the main frame of Fig. 7(a). Here MR was expressed as $\Delta \rho/\rho_0 = (\rho(H) - \rho_0)/\rho_0$, where $\rho(H)$ and $\rho_0$ represent the longitudinal resistivity at a magnetic field $H$ and that at zero field, respectively. One can see that the curve obtained at 20 K reveals a rather different feature compared with the data at temperatures above 25 K. Also the magnitude of MR (obtained at 9 T) at 20 K reached 2 times of that at 25 K giving a sharp drop in the $\Delta \rho/\rho_0 \sim T$ curve when increasing the temperature as revealed in the main frame of Fig. 7. We attribute this behavior to the presence of fluctuant superconductivity in the low temperature region ($\sim$16.3 K-20 K). At temperatures higher than 150 K, the value of MR vanishes to zero gradually.

As for the case in the moderate temperature region, the $\Delta \rho/\rho_0 \sim H$ curve reveals a clear nonlinear behavior. In the inset of Fig. 7(b) we present the data at five typical temperatures in this region. These data were then fitted based on a simple two-band model which gave the following formula

$$\frac{\Delta \rho}{\rho_0} = \frac{(\mu_0 H)^2}{\alpha + \beta \times (\mu_0 H)^2},$$  \hspace{1cm} (3)

with $\alpha$ and $\beta$ the fitting parameters which were related to the conductances and mobilities for the charge carriers in two bands. The fitting results were shown by the solid lines in the inset of Fig. 7(b). It is clear that Eq. 3 can describe our data quite well. This argument can be further confirmed by seeing about the situation of the so-called Kohler plot. The semiclassical transport theory has predicted that the Kohler rule, which can be written as

$$\frac{\Delta \rho}{\rho_0} = F\left(\frac{\mu_0 H}{\rho_0}\right),$$  \hspace{1cm} (4)

will be held if only one isotropic relaxation time is present in a single-band solid-state system. Eq. (4) means that the $\Delta \rho/\rho_0$ vs $\mu_0 H/\rho_0$ curves for different temperatures should be scaled to a universal curve if the Kohler rule is obeyed. The scaling based on the Kohler plot for the present sample is revealed in the inset of Fig. 7(a). An obvious violation of the Kohler rule can be seen on this plot. We attribute this behavior to the presence of a multi-band effect in the present system.

Actually, theoretical researches and angle-resolved photoemission spectroscopic (ARPES) studies have...
shown a rather complicated Fermi surface and energy-band structure in the FeAs-based superconductors. Our data from measuring the Hall effect and MR are consistent with these conclusions.

E. Upper critical field

Finally, we attempted to estimate the upper critical field of the sample with \( x = 0.25 \) from the resistivity data. Temperature dependence of resistivity under different magnetic fields is shown in the main frame of Fig. 8. Similar to that found in the F-doped LaFeAsO polycrystalline samples, the onset transition point, which reflects mainly the upper critical field in the configuration of \( H \parallel ab \)-plane, shifts more slowly than the zero resistivity point to low temperatures under fields. We take a criterion of 95%\( \rho_n \) to determine the onset transition points under different fields, which are presented by the blue open circles in the inset of Fig. 6. From these data we can roughly estimate the upper critical field of this sample based on the Ginzburg-Landau (GL) theory. The following equation have been extract from the GL theory and used successfully on other samples:

\[
H_{c2}(T) = H_{c2}(0) \frac{1 - t^2}{1 + t^2}, \tag{5}
\]

where \( t = T/T_c \) is the reduced temperature and \( H_{c2}(0) \) is the upper critical field at zero temperature. Taking \( T_c = 16.3 \) K and \( H_{c2}(0) \) as the adjustable parameter, the measured data in the inset of Fig. 8 were then fitted using Eq. 5. One can see a quite good fit in the inset of Fig. 8 as revealed by the red solid line. The zero temperature upper critical field was determined to be \( H_{c2}(0) \approx 52 \) T from the fitting process. Actually one can also determine the slope of \( H_{c2}(T) \) near \( T_c \), which is found to be about \(-4.0 \) T/K in the present sample. By using the WHH formula, the value of zero temperature upper critical field \( H_{c2}(0) \) can be estimated through:

\[
H_{c2}(0) = -0.693 T_c \left( \frac{dH_{c2}}{dT} \right)_{T = T_c}. \tag{6}
\]

Taking \( T_c = 16.3 \) K, we get \( H_{c2}(0) \approx 45.1 \) T. Regarding the relatively low value of \( T_c = 16.3 \) K in the present sample, this value of upper critical field \( H_{c2}(0) \) is actually quite high. The slope of \( dH_{c2}(T)/dT \big|_{T_c} \) in the hole-doped sample is clearly larger than that in the electron-doped samples. In the hole-doped \( La_{1-x}Sr_xFeAsO \) superconducting samples, we also found much larger \( dH_{c2}(T)/dT \big|_{T_c} \) when comparing it with the F-doped LaFeAsO samples. This may be understood as due to the higher quasiparticle density of states (DOS) near the Fermi level in the hole-doped samples. In a dirty type-II superconductor, it was predicted that \(-dH_{c2}/dT \big|_{T_c} \propto \gamma_n \) with \( \gamma_n \) the normal state specific heat coefficient which is proportional to the DOS at \( E_F \). It is thus reasonable to ascribe the higher value of \( dH_{c2}/dT \big|_{T_c} \) to higher DOS in the hole-doped samples. Theoretical calculations do show that the DOS in the hole-doped side is larger than that in the electron-doped samples. The measurements on lower critical fields and specific heat in \( Ba_{0.6}K_{0.4}FeAs_2 \) reveal that the superfluid density and the normal state DOS is about 5 to 10 times larger than that in the F-doped REFeAsO system. If the normal state DOS is really larger in the hole-doped systems, higher upper critical fields may be achieved in the hole-doped FeAs-1111 samples provided that the superconducting transition temperature can be improved to the same scale.

IV. CONCLUDING REMARKS

In summary, bulk superconductivity was achieved by substituting \( Pr^{3+} \) with \( Sr^{2+} \) in \( PrFeAsO \) system. A systematic evolution of superconductivity and the lattice constants with doping in hole doped \( Pr_{1-x}Sr_xFeAsO \) was discovered. By doping more \( Sr \) into the parent phase \( PrFeAsO \), the anomaly of resistivity at about 165 K is suppressed gradually and the superconductivity eventually sets in. The \( a \)-axis and \( c \)-axis lattice constants increase monotonically with \( Sr \) concentration. The maximum superconducting transition temperature \( T_c = 16.3 \) K is found to appear around the nominal doping level \( x = 0.20 \sim 0.25 \). The positive Hall coefficient \( R_H \) in a wide temperature range suggests that the hole type charge carriers dominate the conduction in this system. The strong temperature dependence and sign-changing effect of \( R_H \)
were attributed to a multi-band effect and have been interpreted based on a simple two-band model with different types of charge carriers. This argument was further confirmed by the nonlinear field dependence of MR and the violation of the Kohler rule. Interestingly, the slope of the upper critical magnetic field vs. temperature near $T_c$ seems to be much higher than that of the electron-doped samples. This is attributed to the higher DOS in the hole-doped samples than in the electron-doped ones. This may provide a new way to enhance the upper critical field in the hole-doped FeAs-1111 superconductors.

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