SrFeAsF as a parent compound for iron pnictide superconductors

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We have successfully synthesized the fluo-arsenide SrFeAsF, a new parent phase with the ZrCuSiAs structure. The temperature dependence of resistivity and dc magnetization both reveal an anomaly at about \( T_{\text{an}} = 173 \) \( \text{K} \), which may correspond to the structural and/or Spin-Density-Wave (SDW) transition. Interestingly, the Hall coefficient \( R_H \) is positive below \( T_{\text{an}} \), which is opposite to the cases in the two parent phases of FeAs-based systems known so far, i.e., LaFeAsO (\( Ln = \) rare earth elements) and \((\text{Ba}, \text{Sr})\text{Fe}_2\text{As}_2\) where the Hall coefficient \( R_H \) is negative. This strongly suggests that the gapping of the Fermi surface induced by the SDW order leaves one of the hole pockets fully or partially ungapped in SrFeAsF. Our data show that it is possible for the parent phases of the arsenide superconductors to display dominant carriers that are either electronlike or holelike.

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The discovery of superconductivity in the quaternary compound \( \text{LaFeAsO}_{1-x}\text{F}_x \) which is abbreviated as the FeAs-1111 phase, has attracted great attentions in the fields of condensed matter physics and material sciences. The family of the FeAs-based superconductors has been extended rapidly. 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 \( T_c = 55 \sim 56 \) \( \text{K} \) via replacing lanthanum with other rare earth elements\(^{2,3,4,5,6,7}\). Meanwhile, the first hole-doped superconductor \( \text{La}_{1-x}\text{Sr}_x\text{FeAsO} \) with \( T_c \approx 25 \) \( \text{K} \) was discovered\(^{8,9}\) followed with the observation of superconductivity in hole-doped \( \text{Nd}_{1-x}\text{Sr}_x\text{FeAsO} \) and \( \text{Pr}_{1-x}\text{Sr}_x\text{FeAsO} \). Later on, \((\text{Ba, Sr})_x\text{Fe}_2\text{As}_2\) which is denoted as FeAs-122 for simplicity\(^{12,13,14}\), and \( \text{Li}_x\text{FeAs} \) as an infinite layered structure (denoted as FeAs-111) were discovered\(^{15,16,17}\). It is assumed that the superconductivity both in the FeAs-1111 phase and FeAs-122 phase is intimately connected with a Spin-Density-Wave (SDW) anomaly in the FeAs layers\(^{12,18}\). For undoped \( \text{LaFeAsO} \), an SDW-driven structural phase transition around 150 \( \text{K} \) was found\(^{19}\). It seems that any new parent phase will initiate a series of new superconductors by doping it away from the state with features of a bad metal and the SDW order.

In this paper, we report the discovery of a new FeAs-based layered compound SrFeAsF which has the ZrCuSiAs structure. As we know SrZnPF is a compound with like charge carriers in this parent phase. The SrFeAsF samples were prepared using a two-step solid state reaction method, as used for preparing the LaFeAsO samples\(^{20}\). In the first step, SrAs was prepared by reacting Sr flakes (purity 99.9\%) and As grains (purity 99.99\%) at 500 \( ^\circ\text{C} \) for 8 hours and then 700 \( ^\circ\text{C} \) 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\(_3\)F\(_4\) powder (purity 99\%) in stoichiometry as given by the formula SrFeAsF. All the weighing and mixing procedures were performed in a glove box with a protective argon atmosphere. Then the mixture was pressed into pellets and sealed in a quartz tube with an Ar atmosphere of 0.2 bar. The materials were heated up to 950 \( ^\circ\text{C} \) with a rate of 120 \( ^\circ\text{C}/\text{hr} \) and maintained for 60 hours. Then a cooling procedure to room temperature was followed.

The dc magnetization measurements were done with a superconducting quantum interference device (Quantum Design, SQUID, MPMS7). For the magnetotransport measurements, the sample was shaped into a bar with the length of 3 mm, width of 2 mm and thickness of about 0.9 mm. The resistance and Hall effect data were collected using a six-probe technique on the Quantum Design instrument physical property measurement system (PPMS) with magnetic fields up to 9 T. The electric contacts were made using silver paste with the contacting resistance below 0.05 \( \Omega \) at room temperature. The data acquisition was done using a DC mode of the PPMS, which measures the voltage under an alternative DC current and the sample resistivity is obtained by averaging these signals at each temperature. In this way the contacting thermal power is naturally removed. The temperature stabilization was better than 0.1\% and the resolution of the voltmeter was better than 10 nV.

The X-ray diffraction (XRD) pattern for the sample SrFeAsF is shown in Fig. 1. One can see that all the main peaks can be indexed to the FeAs-1111 phase with the tetragonal ZrCuSiAs-type structure. Only small amount of SrF\(_2\) impurity phase was detected. By using the software of Powder-X\(^{22}\), we took a general fit to the XRD data of this sample and the lattice constants were deter-
different temperatures. In the experiment, $3^{+}$ is larger than that of La$^{2+}$.

The structure of the new phase in the present system since the radii of Sr$^{2+}$ is larger than that of La$^{3+}$.

In Fig. 2 (a) we present the temperature dependence of resistivity for the SrFeAsF sample under magnetic fields up to 9 T. A rather large value of the resistivity is observed. An upturn in the low-temperature regime can be seen under all fields, representing a weak semiconductor behavior for the present sample. It is unclear at this moment whether this behavior is intrinsic in nature, or it is due to the weak localization effect, or some other effect. This curve also reveals an anomaly at about $T_{an} = 173$ K, which may correspond to the structural and/or SDW transition, as revealed by the unit cell parameters found in the parent phase of LnFeAsO (Ln = rare earth elements) and (Ba, Sr)Fe$_2$As$_2$. Fig. 2 (b) shows the zero field cooled dc magnetization of the same sample at 5000 Oe. A clear anomaly at about 173 K in the magnetization curve confirms the structural and/or SDW transition observed in the resistivity data. Above 173 K, the magnetization exhibits a rough linear temperature dependence, which may be a common effect in the FeAs-based systems and was explained as due to short range correlation of the local moments.

To get a comprehensive understanding to the conducting carriers in the SrFeAsF phase, we measured the Hall effect of the present sample. The inset of Fig. 3 shows the magnetic field dependence of Hall resistivity ($\rho_{xy}$) at different temperatures. In the experiment, $\rho_{xy}$ was taken as $\rho_{xy} = (\rho(+H) - \rho(-H))/2$ at each point to eliminate the effect of the misaligned Hall electrodes. A nonlinear field dependence of $\rho_{xy}$ was observed in the temperature regime below 75 K, while the linear behavior appeared above 100 K. This may suggest that a multi-band effect or a complicated scattering mechanism (perhaps magnetic related) emerged in the low temperature regime.

The temperature dependence of the Hall coefficient $R_H$ is presented in the main frame of Fig. 3. One can see that $R_H$ remains positive in wide temperature regime and decreases monotonically in the temperature regime below about 160~170 K and it becomes slightly negative above that temperature. The sign changing of $R_H$ and the temperature dependent behavior may be related to the structural and/or SDW transition as revealed by the resistivity data, considering that this change occurred at temperatures close to $T_{an}$. It is worth noting that the positive Hall coefficient $R_H$ in this sample SrFeAsF is quite unique because in the two parent phases of FeAs-based systems known so far, i.e., LnFeAsO (Ln = rare earth elements) and (Ba, Sr)Fe$_2$As$_2$, the Hall coefficient $R_H$ is negative. This strongly suggests that the gaps
obeyed. The scaling based on the Kohler plot of our sample is almost independent of temperature. The strong temperature dependence of $R_H$ below $T_{an}$ in our data suggests either a strong multi-band effect or the variation of the charge carrier densities, or both effects collectively contribute to the Hall signal in the present parent phase of SrFeAsF.

The magnetoresistance (MR) is a very powerful tool to investigate the properties of electronic scattering. Field dependence of MR for the present sample at different temperatures is shown in the main frame in the top panel. A moderate MR effect up to 9% is observed under the field of 9 T at 2 K. Kohler plot of MR is presented in the inset. In the bottom panel of this figure we show the temperature dependence of MR under the field of 9 T. An obvious violation of the Kohler’s rule can be seen from this plot. This behavior may indicate a multi-band effect or a gradual gapping effect to the density of states by the SDW ordering in the present sample. Temperature dependence of MR under the field of 9 T is shown in the bottom part of Fig 4. Rather similar to that observed in the $R_H$ vs $T$ plot, $\Delta \rho/\rho_0$ decreases monotonically in the low temperature regime below about 200 K and a minimum appears around $T_{an}$. This may provide another evidence of the influence of the structural and/or SDW transition on the behavior of the conducting charge carriers.

In summary, a parent phase, namely SrFeAsF, with the ZrCuSiAs structure was synthesized successfully using a two-step solid state reaction method. An anomaly at about 173 K can be observed from the data of the resistivity and dc magnetization, which is ascribed to the structural and/or SDW transition. Also strong Hall effect and moderate MR were observed below $T_{an}$. We found that the Hall coefficient $R_H$ is positive below $T_{an}$, displaying an opposite behavior comparing to the cases

\[
\frac{\Delta \rho}{\rho_0} = \frac{\rho(H) - \rho_0}{\rho_0} = F\left(\frac{H}{\rho_0}\right),
\]

where $\rho(H)$ and $\rho_0$ represents the longitudinal resistivity at a magnetic field $H$ and that at zero field, respectively. Equation (1) means that the $\Delta \rho/\rho_0$ vs $H/\rho_0$ curves for different temperatures, the so-called Kohler plot, should be scaled to a universal curve if the Kohler’s rule is obeyed. The scaling based on the Kohler plot of our sample is more complex than we believed before, and the case in SrFeAsF is that it removes the density of states on the Fermi surfaces induced by the SDW order is more complex than we believed before, and the case in SrFeAsF is that it removes the density of states on some Fermi pockets and may leave one of the hole pockets partially or fully ungapped. Our data clearly show that it is possible for the parent phase to have electron-like or hole-like charge carriers. It is well known that in the conventional metals the Hall coefficient $R_H$ is almost independent of temperature. The strong temperature dependence of $R_H$ below $T_{an}$ in our data suggests either a strong multi-band effect or the variation of the charge carrier densities, or both effects collectively contribute to the Hall signal in the present parent phase of SrFeAsF.

The semiclassical transport theory has predicted that the Kohler’s rule will be held if only one isotropic relaxation time is present in a solid state system. The Kohler’s rule can be written as

\[
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\]

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In summary, a parent phase, namely SrFeAsF, with the ZrCuSiAs structure was synthesized successfully using a two-step solid state reaction method. An anomaly at about 173 K can be observed from the data of the resistivity and dc magnetization, which is ascribed to the structural and/or SDW transition. Also strong Hall effect and moderate MR were observed below $T_{an}$. We found that the Hall coefficient $R_H$ is positive below $T_{an}$, displaying an opposite behavior comparing to the cases

![FIG. 3: (Color online) Temperature dependence of Hall coefficient $R_H$ determined on the present sample SrFeAsF. One can see a monotonic decrease of $R_H$ in the temperature regime below about 160~170 K. Inset: The raw data of the Hall resistivity $\rho_{xy}$ versus the magnetic field $\mu_0 H$ at different temperatures.](image1)

![FIG. 4: (Color online) Field dependence of MR for the present sample at different temperatures is shown in the top panel. A moderate MR effect up to 9% is observed under the field of 9 T at 2 K. Kohler plot of MR is presented in the inset. In the bottom panel of this figure we show the temperature dependence of MR under the field of 9 T.](image2)
in the two parent phases of FeAs-based systems known so far, i.e., LnFeAsO (Ln = rare earth elements) and (Ba, Sr)Fe$_2$As$_2$ where the Hall coefficient $R_H$ is negative. This suggests that the gapping to the Fermi surfaces induced by the SDW order may remove the density of states on some Fermi pockets and leave one of the hole pockets partially or fully ungapped in the present parent phase. Our results clearly show that it is possible for the parent phase to have electron-like or hole-like charge carriers. We also observed a moderate magnetoresistance up to 9% under the field of 9 T. The violation of the Kohler’s rule along with the strong temperature dependence of $R_H$ may suggest a multi-band and/or a spin scattering effect in this system. By doping strontium with lanthanum, we found superconductivity in Sr$_{1-x}$La$_x$FeAsF, which will be presented separately.\textsuperscript{28}

Note added: When we were finalizing this paper, we became aware that a paper was posted on the website on the same day of our submission. That paper reports also the synthesizing of the compound SrFeAsF and a different set of data.\textsuperscript{29}

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