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SrFeAsF as a parent compound for iron pnictide superconductors

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We have successfully synthesized the fluoroarsenide SrFeAsF, which is another parent phase with the ZrCuSiAs structure. The temperature dependence of resistivity and dc magnetization both reveal an anomaly at about $T_{an}=173$ K, which may correspond to the structural and/or spin-density-wave (SDW) transition. Strong Hall effect and moderate magnetoresistance were observed below T_{an}. Interestingly, the Hall coefficient R_H is positive below T_{an}, which is opposite to the cases of the two parent phases of FeAs-based systems known so far, i.e., LnFeAsO (Ln=rare-earth elements) and $(Ba,Sr)Fe_2As_2$, 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 $LaFeAsO_{1-x}F_x$, which is abbreviated as the FeAs-1111 phase, has attracted great attention in the fields of condensed-matter physics and material sciences.[1] 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 $T_c=55-56$ K via replacing lanthanum with other rare-earth elements.[2–7] Meanwhile, the first hole-doped superconductor $La_{1-x}Sr_xFeAsO$ with $T_c \approx 25$ K was discovered,[8,9] followed with the observation of superconductivity in hole-doped $Nd_{1-x}Sr_xFeAsO$ (Ref. 10) and $Pr_{1-x}Sr_xFeAsO$.[11] Later on, $(Ba,Sr)_{1-x}K_xFe_2As_2$, which is denoted as FeAs-122 for simplicity,[12–14] and Li_xFeAs as an infinite layered structure (denoted as FeAs-111) were discovered.[15–17] It is assumed that the superconductivity both in the FeAs-1111 and FeAs-122 phases is intimately connected with a spin-density-wave (SDW) anomaly in the FeAs layers.[12,18] For undoped LaFeAsO, a SDW-driven structural phase transition around 150 K was found.[19] It seems that any different parent phase will initiate a series of different superconductors by doping it away from the state with features of a bad metal and the SDW order.

In this Rapid Communication, we report the discovery of another FeAs-based layered compound SrFeAsF which has the ZrCuSiAs structure. As we know SrZnPF is a compound with the ZrCuSiAs structure.[20] We replace the ZnP sheets with FeAs sheets and get another compound of SrFeAsF. The compound SrFeAsF has the tetragonal space group $P4/nmm$ at 300 K. Both the resistivity and the dc magnetic susceptibility exhibit a clear anomaly at about 173 K, which is attributed to the structural and/or SDW transition. Surprisingly, a positive Hall coefficient R_H has been found implying a dominant conduction by holelike 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.[21] In the first step, SrAs was prepared by reacting Sr flakes (purity of 99.9%) and As grains (purity of 99.99%) at 500 °C for 8 h and then at 700 °C for 16 h. They were sealed in an evacuated quartz tube when reacting. Then the resultant precursors were thoroughly grounded together with Fe (purity of 99.95%) and FeF_3 powders (purity of 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 °C with a rate of 120 °C/h and maintained for 60 h. Then a cooling procedure to room temperature was followed.

The dc magnetization measurements were done with a superconducting quantum interference device (SQUID) (Quantum Design, 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 Ω 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 a small amount of the SrF_2 impurity phase was detected. By using the software POWDER-X,[22] we took a general fit to the XRD data of this sample, and the lattice constants were determined to be $a=4.004$ Å and $c=8.971$ Å. It is clear that the a-axis lattice constant of this parent phase is slightly smaller than that of the LaFeAsO system while the c-axis one is much larger,[1,21] indicating a completely different phase in the present system since the radii of Sr^{2+} are larger than that of La^{3+}.

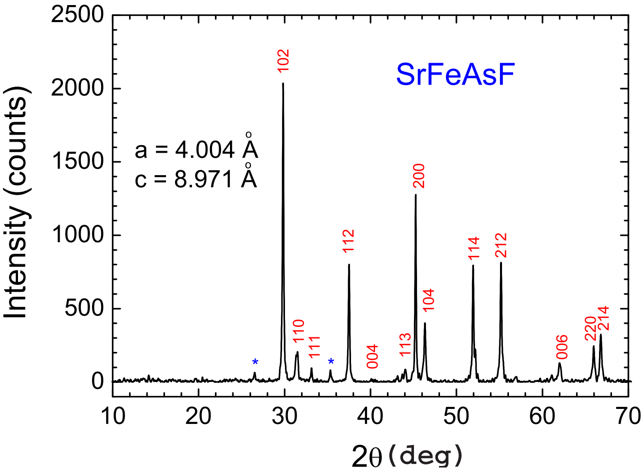

FIG. 1. (Color online) X-ray diffraction patterns for the SrFeAsF sample. One can see that all the main peaks can be indexed to the tetragonal ZrCuSiAs-type structure. The asterisks indicate the little impurities from the SrF_2 phase.

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 semiconductorlike 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 has been found in the parent phase of LnFeAsO (Ln=rare-earth elements) and $(Ba,Sr)Fe_2As_2$.[1,12] Figure 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.[23]

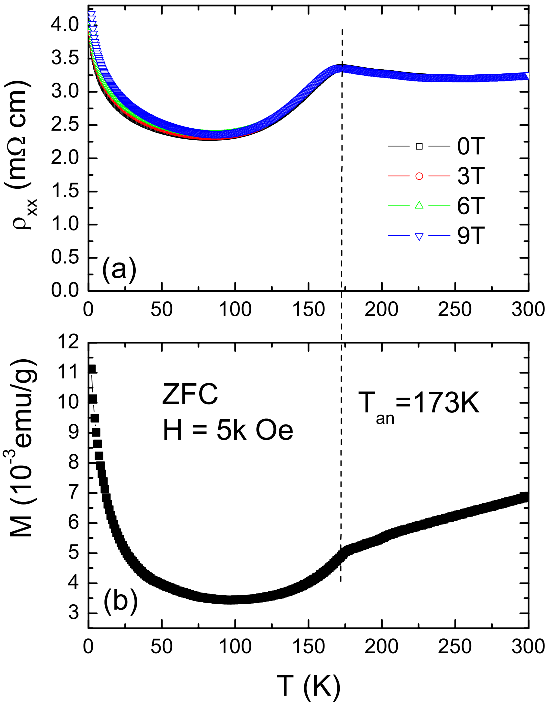

FIG. 2. (Color online) (a) Temperature dependence of resistivity for the SrFeAsF sample under magnetic fields of up to 9 T. A clear anomaly at about $T_{an}=173$ K can be observed. (b) Temperature dependence of dc magnetization for the zero-field-cooling (ZFC) process at a magnetic field of $H=5000$ Oe. We can also see an anomaly at the same temperature in the $M(T)$ curve.

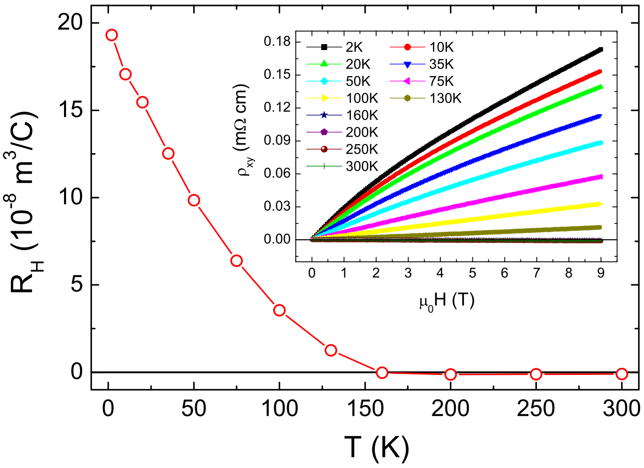

FIG. 3. (Color online) Temperature dependence of Hall coefficient R_H determined on the present sample SrFeAsF. One can see a monotonic decrease in R_H in the temperature regime below about 160–170 K. Inset: the raw data of the Hall resistivity ρ_{xy} versus the magnetic field $\mu_0 H$ at different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

To get a comprehensive understanding of 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 (ρ_{xy}) at different temperatures. In the experiment, ρ_{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 ρ_{xy} was observed in the temperature regime below 75 K, while the linear behavior appeared above 100 K. This may suggest that a multiband 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 the wide temperature regime and decreases monotonically in the temperature regime below about 160–170 K, and it becomes slightly negative above that temperature. The change in sign 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 the 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 $(Ba,Sr)Fe_2As_2$, the Hall coefficient R_H is negative. This strongly suggests that the gapping to the Fermi surfaces induced by the SDW order is more complex than we believed

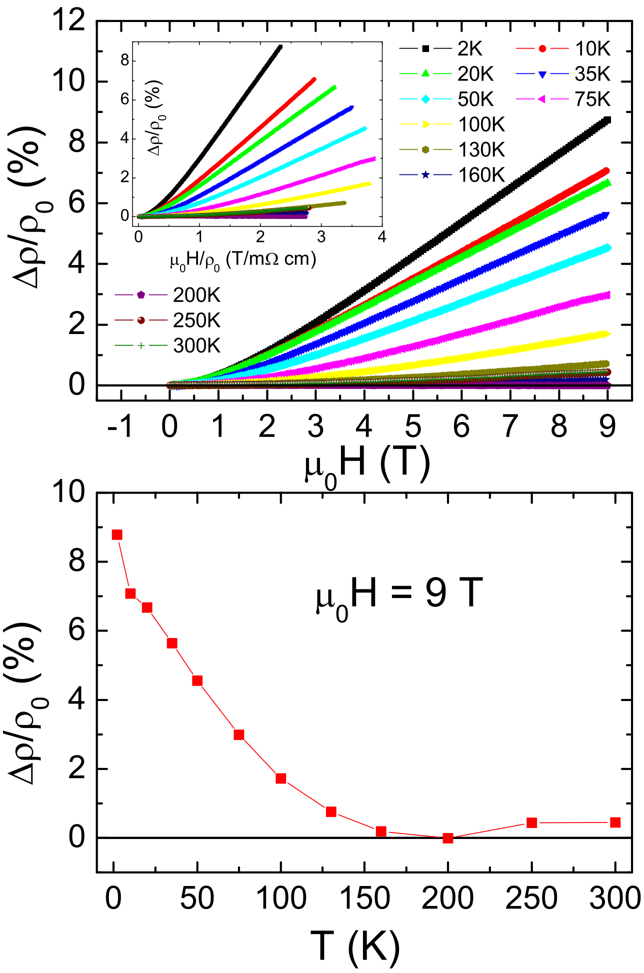

FIG. 4. (Color online) Field dependence of MR for the present sample at different temperatures is shown in the top panel. A moderate MR effect of up to 9% is observed under the field of 9 T at 2 K. Kohler plot of MR is presented in the inset. In the bottom panel of this figure we show the temperature dependence of MR under the field of 9 T.

before, and in the case of SrFeAsF 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 electronlike or holelike 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 multiband effect or the variation in 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 for investigating the properties of electronic scattering.[24,25] Field dependence of MR for the present sample at different temperatures is shown in the main frame in the top part of Fig. 4. One can see a moderate MR effect of up to 9% under the field of 9 T at 2 K. This is a rather large magnitude compared with the F-doped LnFeAsO samples.[21,26] The semiclassical transport theory has predicted that the Kohler rule will be held if only one isotropic relaxation time is present in a solid-state system.[27] The Kohler rule can be written as

$$\frac{\Delta\rho}{\rho_0} = \frac{\rho(H) - \rho_0}{\rho_0} = F\left(\frac{H}{\rho_0}\right), \qquad (1)$$

where $\rho(H)$ and ρ_0 represent the longitudinal resistivity at a magnetic field H and at zero field, respectively. Equation (1) means that the $\Delta\rho/\rho_0$ vs H/ρ_0 curves for different temperatures, the so-called Kohler plot, should be scaled to a universal curve if the Kohler rule is obeyed. The scaling based on the Kohler plot of our sample is revealed in the inset of the top part of Fig. 4. An obvious violation of the Kohler rule can be seen on this plot. This behavior may indicate a multiband 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 more 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 compared to the cases of the two parent phases of FeAs-based systems known so far, i.e., LnFeAsO (Ln=rare-earth elements) and $(Ba,Sr)Fe_2As_2$ 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 electronlike or holelike charge carriers. We also observed a moderate magnetoresistance of up to 9% under the field of 9 T. The violation of the Kohler rule along with the strong temperature dependence of R_H may suggest a multiband and/or a spin scattering effect in this system. By doping strontium with lanthanum, we found superconductivity in $Sr_{1-x}La_xFeAsF$, which will be presented separately.[28]

Note added. When we were finalizing this Rapid Communication, 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.[29]

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[1] Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, J. Am. Chem. Soc. **130**, 3296 (2008).

[2] X. H. Chen, T. Wu, G. Wu, R. H. Liu, H. Chen, and D. F. Fang, Nature (London) **453**, 761 (2008).

[3] G. F. Chen, Z. Li, D. Wu, G. Li, W. Z. Hu, J. Dong, P. Zheng, J. L. Luo, and N. L. Wang, Phys. Rev. Lett. **100**, 247002 (2008).

[4] Z. A. Ren, J. Yang, W. Lu, W. Yi, G.-C. Che, X.-L. Dong, L.-L. Sun, and Z.-X. Zhao, Mater. Res. Innovations **12**, 105 (2008).

[5] Z. A. Ren, W. Lu, J. Yang, W. Yi, X. L. Shen, Z. C. Li, G. C. Che, X. L. Dong, L. L. Sun, F. Zhou, and Z. X. Zhao, Chin. Phys. Lett. **25**, 2215 (2008).

[6] Peng Cheng, Lei Fang, Huan Yang, Xiyu Zhu, Gang Mu, Huiqian Luo, Zhaosheng Wang, and Hai-Hu Wen, Sci. China, Ser. G **51**, 719 (2008).

[7] Cao Wang, Linjun Li, Shun Chi, Zengwei Zhu, Zhi Ren, Yuke Li, Yuetao Wang, Xiao Lin, Yongkang Luo, Shuai Jiang, Xiangfan Xu, Guanghan Cao, and Zhu'an Xu, Europhys. Lett. **83**, 67006 (2008).

[8] H. H. Wen, G. Mu, L. Fang, H. Yang, and X. Zhu, Europhys. Lett. **82**, 17009 (2008).

[9] Gang Mu, Lei Fang, Huan Yang, Xiyu Zhu, Peng Cheng, and Hai-Hu Wen, arXiv:0806.2104 (unpublished).

[10] Karolina Kasperkiewicz, Jan-Willem G. Bos, Andrew N. Fitch, Kosmas Prassides, and Serena Margadonna, arXiv:0809.1755 (unpublished).

[11] Gang Mu, Bin Zeng, Xiyu Zhu, Fei Han, Peng Cheng, Bing Shen, and Hai-Hu Wen, arXiv:0810.0986 (unpublished).

[12] M. Rotter, M. Tegel, D. Johrendt, I. Schellenberg, W. Hermes, and R. Pottgen, Phys. Rev. B **78**, 020503(R) (2008).

[13] M. Rotter, M. Tegel, and D. Johrendt, Phys. Rev. Lett. **101**, 107006 (2008).

[14] K. Sasmal, B. Lv, B. Lorenz, A. M. Guloy, F. Chen, Y. Y. Xue, and C. W. Chu, Phys. Rev. Lett. **101**, 107007 (2008).

[15] X. C. Wang, Q. Q. Liu, Y. X. Lv, W. B. Gao, L. X. Yang, R. C. Yu, F. Y. Li, and C. Q. Jin, arXiv:0806.4688 (unpublished).

[16] Joshua H. Tapp, Zhongjia Tang, Bing Lv, Kalyan Sasmal, Bernd Lorenz, Paul C. W. Chu, and Arnold M. Guloy, Phys. Rev. B **78**, 060505(R) (2008).

[17] Michael J. Pitcher, Dinah R. Parker, Paul Adamson, Sebastian J. C. Herkelrath, Andrew T. Boothroyd, Richard M. Ibberson, Michela Brunelli, and Simon J. Clarke, Chem. Commun. (Cambridge) (to be published).

[18] J. Dong, H. J. Zhang, G. Xu, Z. Li, G. Li, W. Z. Hu, D. Wu, G. F. Chen, X. Dai, J. L. Luo, Z. Fang, and N. L. Wang, Europhys. Lett. **83**, 27006 (2008).

[19] Clarina de la Cruz, Q. Huang, J. W. Lynn, Jiying Li, W. Ratcliff II, J. L. Zarestky, H. A. Mook, G. F. Chen, J. L. Luo, N. L. Wang, and Pengcheng Dai, Nature (London) **453**, 899 (2008).

[20] Houria Kabbour, Laurent Cario, and Florent Boucher, J. Mater. Chem. **15**, 3525 (2005).

[21] Xiyu Zhu, Huan Yang, Lei Fang, Gang Mu, and Hai-Hu Wen, Supercond. Sci. Technol. **21**, 105001 (2008).

[22] C. Dong, J. Appl. Crystallogr. **32**, 838 (1999).

[23] G. M. Zhang, Y. H. Su, Z. Y. Lu, Z. Y. Weng, D. H. Lee, and T. Xiang, arXiv:0809.3874 (unpublished).

[24] Q. Li, B. T. Liu, Y. F. Hu, J. Chen, H. Gao, L. Shan, H. H. Wen, A. V. Pogrebnyakov, J. M. Redwing, and X. X. Xi, Phys. Rev. Lett. **96**, 167003 (2006).

[25] H. Yang, Y. Liu, C. G. Zhuang, J. R. Shi, Y. G. Yao, S. Massidda, M. Monni, Y. Jia, X. X. Xi, Q. Li, Z. K. Liu, Q. R. Feng, and H. H. Wen, Phys. Rev. Lett. **101**, 067001 (2008).

[26] Peng Cheng, Huan Yang, Ying Jia, Lei Fang, Xiyu Zhu, Gang Mu, and Hai-Hu Wen, Phys. Rev. B **78**, 134508 (2008).

[27] J. M. Ziman, *Electrons and Phonons*, Classics Series (Oxford University Press, New York, 2001).

[28] Xiyu Zhu, Fei Han, Peng Cheng, Gang Mu, Bing Shen, and Hai-Hu Wen, arXiv:0810.2531 (unpublished).

[29] M. Tegel, S. Johansson, V. Weiss, I. Schellenberg, W. Hermes, R. Poettgen, and D. Johrendt, arXiv:0810.2120 (unpublished).