Superconductivity induced by U-doping in the SmFeAsO system

Bo Huang, Jijun Yang, Jun Tang, Jiali Liao, Yuanyou Yang, Ning Liu, Gang Mu, Tao Hu, Xiaoping Shen, and Donglai Feng

1Key Laboratory of Radiation Physics and Technology (Sichuan University), Ministry of Education; Institute of Nuclear Science and Technology, Sichuan University Chengdu 610064, P. R. China.
2State Key Laboratory of Functional Materials for Informatics, Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences 865 Changning Road, Shanghai 200050, China
3State Key Laboratory of Surface Physics, Department of Physics, and Advanced Materials Laboratory, Fudan University, Shanghai 200433, China

(Dated: February 22, 2013)

Through partial substitution of Sm by U in SmFeAsO, a different member of the family of iron-based superconductors was successfully synthesized. X-ray diffraction measurements show that the lattice constants along a-axis and c-axis are both squeezed through U doping, indicating a successful substitution of U at the Sm site. The parent compound shows a strong resistivity anomaly near 150 K, associated with spin-density-wave (SDW) instability. U doping suppresses this instability and leads to a transition to the superconducting state at temperature up to 49 K. Magnetic measurements confirm the bulk superconductivity in this system. For the sample with a doping level $x = 0.2$, the external magnetic field suppresses the onset temperature very slowly, indicating a rather high upper critical field. In addition, the Hall effect measurements show that U clearly dopes electrons into the material.

PACS numbers: 74.70.Dd, 74.62.Dh, 74.25.Dw, 74.70.Xa

The discovery of iron-based superconductors spawned a new research upsurge of superconductors. These compounds became ideal superconductors due to their amazing properties different from conventional BCS superconductors and the cuprates. The huge family of iron-based superconductors can be classified as 1111 type, 122 type, 111 type, 11 type, 21311 type, and so on, according to their structure features. Among these categories, the 1111-type compounds are found to have a tetragonal ZrCuSiAs-type crystal structure and the highest critical transition temperature ($T_c$). Different element substitutions have been successfully performed by researchers to induce superconductivity in this system, e.g., O→F, Ln (Ln = rare-earth elements)→Th⁴⁺/Sm³⁺, Fe→Co¹⁺/Ni²⁺/As²⁻, Lu→P³⁺. Generally speaking, the effect of element substitution is to adjust the charge carrier concentration and the structural parameters. These two factors seem to be crucial to enhance $T_c$ in iron-based superconductors. The indirect substitution (e.g. O→F) is found to have more advantages in achieving a higher $T_c$ than the direct substitution (e.g. Fe→Co). However, it is difficult to control the amount of fluorine in the system, especially in the process of single-crystal growth. Similar problem also remains for other indirectly doped 1111-systems, i.e., the alkaline-earth elements (Sr, Ca) substitution at the Ln sites (Ln=La, Pr, Nd, Eu) by the 5f element thorium (Th) was found to be another effective indirect substitution, which can also induce superconductivity with $T_c$ above 50 K in Ln₃₋ₓThₓFeAsO₇-δ. However, there is still a large space to improve the volume fraction of magnetic shielding in Th-doped systems.

Obviously, it is requisite to explore alternative ways to introduce high-$T_c$ superconductivity in a easily-controlled way and with a high volume fraction. It has been found that the FeAs₂-lattices in SmFeAsO can form a regular tetrahedron naturally, which is profitable to obtain the high $T_c$. In this sense, another 5f element uranium (U) is expected to be a better dopant on Sm site, because the radius of U⁴⁺ is very close to that of Sm³⁺ so that to minimize the lattice mismatch. In this Rapid Communication, we report the successful synthesis and characterization of another 5f element the uranium-doped superconducting material Sm$_{1-x}$U$_x$FeAsO with $T_c$ as high as 49 K. Bulk superconductivity is confirmed by resistivity and magnetization measurements. A clear evolution of the charge carriers is evidenced by the Hall effect data. Our results suggest that there many opportunities to find different superconductors in this field.

The polycrystalline samples of Sm$_{1-x}$U$_x$FeAsO were synthesized by solid state reaction in an evacuated quartz tube. The starting materials are SmAs, U$_3$O$_8$, FeAs, Fe and Fe$_2$O$_4$, with the purity of higher than 99.95%. SmAs and FeAs were pre-synthesized by reacting Sm tapes and Fe powders with As grains at high temperature. U$_3$O$_8$ was acquired from the decomposition of UO$_2$(NO$_3$)$_2$ under 800 °C. The raw materials were mixed well according to the stoichiometry, and then pressed into pellets in an argon-filled glove box (both H$_2$O and O$_2$ are limited below 0.1 ppm). The pressed pellets were sealed in an evacuated quartz tube, and slowly heated to 1180 °C, holding for 90 h. Finally the samples were furnace cooled to room temperature.

Powder x-ray diffraction (XRD) measurements was performed at room temperature with DX-2500 X-ray diffractometer using Cu Kα radiation from 20° to 80°
with a step of 0.03°. The dc magnetization was measured with a superconducting quantum interference device (Quantum Design, MPMS-7T). The resistivity and Hall effect measurements were performed using a physical property measurement system (Quantum Design, PPMS-9T) with magnetic fields up to 9 T. The electrical resistivity was measured by a standard four-probe technique using silver paste electrodes.

Figure 1 shows the powder XRD pattern of Sm\(_{1-x}\)U\(_x\)FeAsO samples with doping level \(x = 0, 0.1, 0.2\). Small amount of impurity phases have been detected on the doped samples, which are denoted by red asterisks.

The resistivity of Sm\(_{1-x}\)U\(_x\)FeAsO is shown in Fig. 2(a) as a function of temperature. The resistivity of the undoped sample shows an anomaly at about 150 K, which is a quite common feature in the 1111-type parent compounds associated with structural phase transition and antiferromagnetic spin-density-wave (SDW) instability\(^{22,23}\). Such an anomalous feature is suppressed by U doping, accompanying the emergence of superconductivity in low temperatures. From the data we can see the onset transition temperatures for the samples with \(x = 0.1\) and 0.2 are 47 K and 49 K, respectively, as clearly revealed in the inset of Fig. 2(a). For \(x = 0.1\), the resistivity in the normal state shows a linear dependence with temperature below about 120 K, while a clear negative-curvature is observed in the wide temperature range. This behavior has been reported in other electron-doped 1111 systems\(^{7,8,13}\), which may reflect the presence of unconventional scattering mechanism in this system. With the increase of doping content, the negative-curvature feature is weakened, as shown in the data with \(x = 0.2\). Such an interesting evolution needs more investigations in the future.

The U-doped samples were checked by magnetic susceptibility measurements. Here we show the data for \(x = 0.2\) in Fig. 2(b) as an example. The measurements were carried out under a magnetic field of 20 Oe in zero-
field-cooled and field-cooled processes. One can see clear diamagnetic signals in the low temperature region. The onset transition temperature is determined to be about 46 K for this sample, which corresponds well to the middle point of the resistive transition. The magnitude of the dc susceptibility suggests the bulk superconductivity in the present sample. We note here that the volume fraction of magnetic shielding in the present system is clearly improved compared with the Th-doped systems.

To obtain the information of upper critical field, the resistivity data near the superconducting transition were collected under different magnetic fields. As shown in Fig. 3, the transitions for the sample with \(x = 0.2\) are suppressed gradually by the field. It has been pointed out that the onset transition point mainly reflects the upper critical field in the configuration of \(H||ab\)-plane. Taking a criterion of 95\% \(\rho_n\), the onset transition temperatures under different fields are determined and plotted in the inset of Fig. 3. From these data, we can get the slope of \(H_{c2}(T)\) near \(T_c\): \(\frac{dH_{c2}/dT}{T=T_c}\approx -7.4\) T/K. This value is comparable to other 1111 system with similar \(T_c\).\(^{27,28}\)

Then the simple Werthamer-Helfand-Hohenberg (WHH) formula internet\(^{29}\): \(H_{c2}(0) = -0.693 \times T_c\left(\frac{dH_{c2}/dT}{T=T_c}\right)_{T=T_c}\) is adopted to estimate the upper critical field to be 250 T.

In order to get more information about the conducting carriers in the samples, we also carried out the Hall-effect measurements. Figure 4 shows the magnetic field dependence of Hall resistivity \(\rho_{xy}\) at different temperatures for the samples with \(x = 0, 0.1,\) and 0.2, respectively. The value of \(\rho_{xy}\) was taken as \(\rho_{xy} = [\rho(+H) - \rho(-H)]/2\) at each point to eliminate the effect of the misaligned Hall electrodes. For the samples with \(x = 0.1\) and 0.2, almost all the curves show a good linearity versus the magnetic field and \(\rho_{xy}\) is negative at all temperatures above the critical temperature, indicating domination of electron-like charge carriers in the normal-state conduction. For the parent sample, however, the linear behavior can only be observed in the temperatures above 150 K, suggesting a drastic change of the conducting conditions during the structural and antiferromagnetic transitions at 150 K.

Temperature dependence of Hall coefficient \(R_H\) is shown in Fig. 5. It is clear that the absolute value of
$R_H$ decreases with increasing $x$, indicating that U doping leads to an increase of the electron concentration. For the sample $x = 0$, the Hall coefficient shows a pronounced change at about 150 K, which can also be originated from the structural and antiferromagnetic transitions. We note that $R_H$ of the superconducting samples also shows a sizable temperature dependent behavior, as enlarged in the inset of Fig. 5. This may reveal a trace of multi-band effect in the present system.

In summary, we found that U doping is effective in inducing superconductivity in SmFeAsO system. The highest critical transition temperature of about 49 K was confirmed by resistivity and magnetic susceptibility measurements. X-ray diffraction patterns indicate that the obtained materials have formed the ZrCuSiAs-type crystal structure. The systematic evolution of the lattice constants with doping demonstrated that the U ions have been successfully doped into the sites of Sm. The upper critical field is estimated for the sample with $x = 0.2$. Hall effect measurements show a clear electron-doping process with the increasing U concentration. Our results demonstrate a new and better approach to introduce superconductivity in the 1111 system, where the doping content is easier to control and the volume fraction of magnetic shielding is improved. The present system may be suitable for the single-crystal growth and in-depth research in the next step.

This work was supported by National Natural Science Foundation of China (No. 91226108, 11274234 and 11204338), the International Thermonuclear Experimental Reactor (ITER) Program Special (Grant No. 2011GB108005), the Program for New Century Excellent Talents in University (No. NCET-10-0571), the Knowledge Innovation Project of Chinese Academy of Sciences (KJCX2-EW-W11), the National Fund of China for Fostering Talents in Basic Science (J1210004), and State Key Laboratory of Surface Physics, Fudan University (No.KS2011-02).

* Electronic address: tangjun@scu.edu.cn
† Electronic address: mugang@mail.sim.ac.cn

1. Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, J. Am. Chem. Soc. 130, 3296 (2008).
2. 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).
3. Z. A. Ren, J. Yang, W. Lu, W. Yi, G. C. Che, X. L. Dong, L. L. Sun, and Z. X. Zhao, Mater. Res. Innov. 12, 105 (2008).
4. G. F. Chen, Z. Li, D. Wu, J. Dong, G. Li, W. Z. Hu, P. Zheng, J. L. Luo, and N. L. Wang, Chin. Phys. Lett. 25, 2235 (2008).
5. X. H. Chen, T. Wu, G. Wu, R. H. Liu, H. Chen, and D. F. Fang, Nature 453, 761 (2008).
6. P. Cheng, L. Fang, H. Yang, X. Y. Zhu, G. Mu, H. Q. Luo, Z. S. Wang, and H. H. Wen, Sci. China, Ser. G. 51, 719 (2008).
7. C. Wang, L. J. Li, S. Chi, Z. W. Zhu, Z. Ren, Y. K. Li, Y. T. Wang, X. Lin, Y. K. Luo, S. Jiang, X. F. Xu, G. H. Cao, and Z. A. Xu, Europhys. Lett. 83, 67006 (2008).
8. L. J. Li, Y. K. Li, Z. Ren, Y. K. Luo, X. Lin, M. He, Q. Tao, Z. W. Zhu, G. H. Cao, and Z. A. Xu, Phys. Rev. B. 78, 132506 (2008).
9. M. Xu, F. Chen, C. He, H. W. Ou, J. F. Zhao, and D. L. Feng, Chem. Mater. 20, 7201 (2008).
10. H. H. Wen, G. Mu, L. Fang, H. Yang, and X. Zhu, Europhys. Lett. 82, 17009 (2008).
11. K. Kasperkiewicz, J. W. Bos, A. N. Fitch, K. Prassides, and S. Margadonna, Chem. Commun. 707 (2009).
12. G. Mu, B. Zeng, X. Zhu, F. Han, P. Cheng, B. Shen, and H. H. Wen, Phys. Rev. B. 79, 104501 (2009).
13. A. S. Sefat, A. Huq, M. A. McGuire, R. Jin, B. C. Sales, D. Mandrus, L. M. D. Cranswick, P. W. Stephens, and K. H. Stone, Phys. Rev. B. 78, 104505 (2008).
14. C. Wang, Y. K. Li, Z. W. Zhu, S. Jiang, X. Lin, Y. K. Luo, S. Chi, L. J. Li, Z. Ren, M. He, H. Chen, Y. T. Wang, Q. Tao, G. H. Cao, and Z. A. Xu, Phys. Rev. B. 79, 054521 (2009).
15. G. Cao, S. Jiang, X. Lin, C. Wang, Y. Li, Z. Ren, Q. Tao, C. Feng, J. Dai, Z. A. Xu, and F. C. Zhang, Phys. Rev. B. 79, 174505 (2009).
16. Y. L. Chen, C. H. Cheng, Y. J. Cui, H. Zhang, Y. Zhang, Y. Yang, and Y. Zhao, J. Am. Chem. Soc. 131, 10338 (2009).
17. Y. Qi, L. Wang, Z. Gao, D. Wang, X. Zhang, Z. Zhang, and Y. Ma, Phys. Rev. B. 80, 045402 (2009).
18. C. Wang, S. Jiang, Q. Tao, Z. Ren, Y. Li, L. Li, C. Feng, J. Dai, G. Cao, and Z. A. Xu, Europhys. Lett. 86, 47002 (2009).
19. C. H. Lee, A. Iyo, H. Eisaki, H. Kito, M. T. F. Diaz, T. Ito, K. Kihou, H. Matsuhata, M. Braden, and K. Yamada, J. Phys. Soc. Jpn. 77, 083704 (2008).
20. J. Q. Yan, S. Nandi, J. L. Zarestky, W. Tian, A. Kreyssig, B. Jensen, A. Kracher, K. W. Dennis, R. J. McQueeney, A. I. Goldman, R. W. McCallum, and T. A. Lograsso, Appl. Phys. Lett. 95, 222504 (2009).
21. R. H. Liu, G. Wu, T. Wu, D. F. Fang, H. Chen, S. Y. Li, K. Liu, Y. L. Xie, F. Wang, R. L. Yang, L. Ding, C. He, D. L. Feng, and X. H. Chen, Phys. Rev. Lett. 101, 087001 (2008).
22. J. Dong, H. J. Zhang, G. Xu, Z. Li, G. Li, W. Zhu, D. Wu, G. F. Chen, X. Dai, J. L. Luo, Z. Fang, and N. L. Wang, Europhys. Lett. 83, 27006 (2008).
23. C. de la Cruz, Q. Huang, J. W. Lynn, J. Li, W. Ratcliff II, J. L. Zarestky, H. A. Mook, G. F. Chen, J. L. Luo, N. L. Wang, and P. Dai, Nature 453, 899 (2008).
24. 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).
25. P. Cheng, H. Yang, Y. Jia, L. Fang, X. Y. Zhu, G. Mu, and H. H. Wen, Phys. Rev. B. 78, 134508 (2008).
26. X. Zhu, H. Yang, L. Fang, G. Mu, and H. H. Wen, Supercond. Sci. Technol. 21, 105001 (2008).
27. Y. Jia, P. Cheng, L. Fang, H. Luo, H. Yang, C. Ren, L. Shen, C. Gu, and H. H. Wen, Appl. Phys. Lett. 93, 032503 (2008).
28. H. S. Lee, M. Bartkowiak, J. H. Park, J. Y. Lee, J. Y. Kim,
N. H. Sung, B. K. Cho, C. U. Jung, J. S. Kim, and H. J. Lee, Phys. Rev. B. 80, 144512 (2009).

N. R. Werthamer, E. Helfand, and P. C. Hohenberg, Phys. Rev. 147, 295 (1966).