

Superconductivity induced by U doping in the SmFeAsO system

Bo Huang,¹ Jijun Yang,¹ Jun Tang,^{1,*} Jiali Liao,¹ Yuanyou Yang,¹ Ning Liu,¹ Gang Mu,^{2,†} Tao Hu,²
Xiaoping Shen,³ and Donglai Feng³

¹Key Laboratory of Radiation Physics and Technology, Ministry of Education, Institute of Nuclear Science and Technology,
Sichuan University, Chengdu 610064, People's Republic of 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, People's Republic of China

³State Key Laboratory of Surface Physics, Department of Physics, and Advanced Materials Laboratory,
Fudan University, Shanghai 200433, People's Republic of China

(Received 26 December 2012; revised manuscript received 31 January 2013; published 13 February 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 the a and c axes 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 instability. U doping suppresses this instability and leads to a transition to the superconducting state at temperatures up to 49 K. Magnetic measurements confirm the bulk superconductivity in this system. For the sample with a doping level of $x = 0.2$, 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.

DOI: [10.1103/PhysRevB.87.060501](https://doi.org/10.1103/PhysRevB.87.060501)

PACS number(s): 74.70.Dd, 74.62.Dh, 74.25.Dw, 74.70.Xa

The discovery of iron-based superconductors spawned an upsurge in the research of superconductors.¹ These compounds became ideal superconductors due to amazing properties that are different from conventional BCS superconductors and the cuprates. The huge family of iron-based superconductors can be classified as 1111, 122, 111, 11, 21311 types, 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., $O \rightarrow F$,¹⁻⁶ Ln (Ln = rare-earth elements) \rightarrow Th (Refs. 7-9)/Sr (Refs. 10-12), $Fe \rightarrow Co$ (Refs. 13 and 14)/Ni (Ref. 15)/Ir (Refs. 16 and 17), $As \rightarrow P$.¹⁸ 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.¹⁹ Indirect substitution (e.g., $O \rightarrow F$) is found to have more advantages in achieving a higher T_c than direct substitution (e.g., $Fe \rightarrow Co$). However, it is difficult to control the amount of fluorine in the system, especially in the process of single-crystal growth.²⁰ Similar problems also remain for other indirectly doped 1111 systems, i.e., the substitution of alkaline-earth elements (Sr, Ca) at the Ln sites ($Ln = La, Pr, Nd$).¹⁰⁻¹² Doping on the site of Ln ($Ln = Gd, Tb, Nd$) 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 $Ln_{1-x}Th_xFeAsO$.⁷⁻⁹ However, there are still large improvements to be made to 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 an easily controlled way and with a high volume fraction. It has been found that the FeAs₄ lattices in SmFeAsO can naturally form a regular tetrahedron, which is beneficial to obtain high T_c .¹⁹ In this sense, another 5f element uranium (U) is expected to be a

better dopant on the Sm site, because the radius of U^{4+} is very close to that of Sm^{3+} so as 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 $Sm_{1-x}U_xFeAsO$ 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 $Sm_{1-x}U_xFeAsO$ were synthesized by a solid state reaction in an evacuated quartz tube. The starting materials are SmAs, U_3O_8 , FeAs, Fe, and Fe_2O_3 , with a purity of higher than 99.95%. SmAs and FeAs were presynthesized by reacting Sm tapes and Fe powders with As grains at high temperature. U_3O_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_2O 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 a DX-2500 x-ray diffractometer using Cu $K\alpha$ 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 $Sm_{1-x}U_xFeAsO$ ($x = 0, 0.1, 0.2$) samples. The main diffraction peaks of the three samples can all be well indexed based on the tetragonal

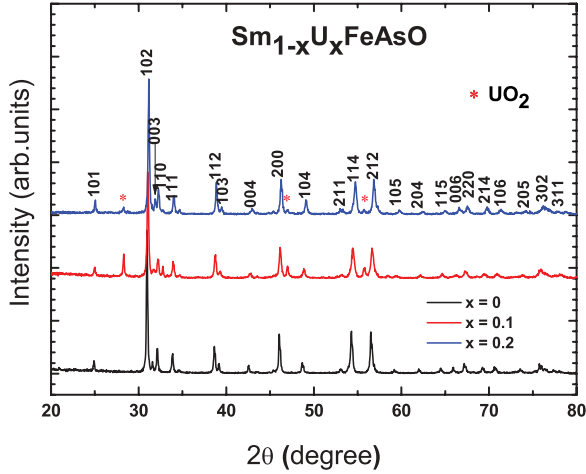


FIG. 1. (Color online) X-ray diffraction patterns for $\text{Sm}_{1-x}\text{U}_x\text{FeAsO}$ samples with doping levels $x = 0, 0.1$, and 0.2 . A small amount of impurity phases has been detected on the doped samples, which are denoted by red asterisks.

ZrCuSiAs -type structure with the space group $P4/nmm$. The refined lattice parameters are $a = 3.9396(7)$ Å and $c = 8.4921(4)$ Å for the parent compound, basically consistent with the previously reported values.⁵ The tiny peaks marked by the asterisks are contributed by the secondary UO_2 phase, which is the main impurity phase in the U-doped samples. The presence of an impurity phase also indicates that the actual doping level is less than the nominal one. We note here that all the doping values in this Rapid Communication are nominal ones. The refined lattice constants for $x = 0.1$ and 0.2 are $a = 3.9315(7)$ Å, $c = 8.4654(2)$ Å and $a = 3.9214(2)$ Å, $c = 8.4165(7)$ Å, respectively. We can see that, by substituting U into Sm sites, both the lattice constants along the a and c axes shrink. This tendency is similar to the case of doping F into the O site in the Ln_2O_2 layers,^{1-3,21} but different from the case of substituting Ln by Th atoms,⁷⁻⁹ where Th substitution expands the crystal lattice along the a axis and squeezes it along the c axis. This phenomenon is most likely due to the different relative radii of the doped ions. We emphasize that the substantial and systematical change in lattice constants indicates that uranium is successfully incorporated in the lattice.

The resistivity of $\text{Sm}_{1-x}\text{U}_x\text{FeAsO}$ 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 the 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 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 temperatures 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,^{7,24,25} which may reflect the presence of an unconventional scattering mechanism in this system. With the increase of doping content,

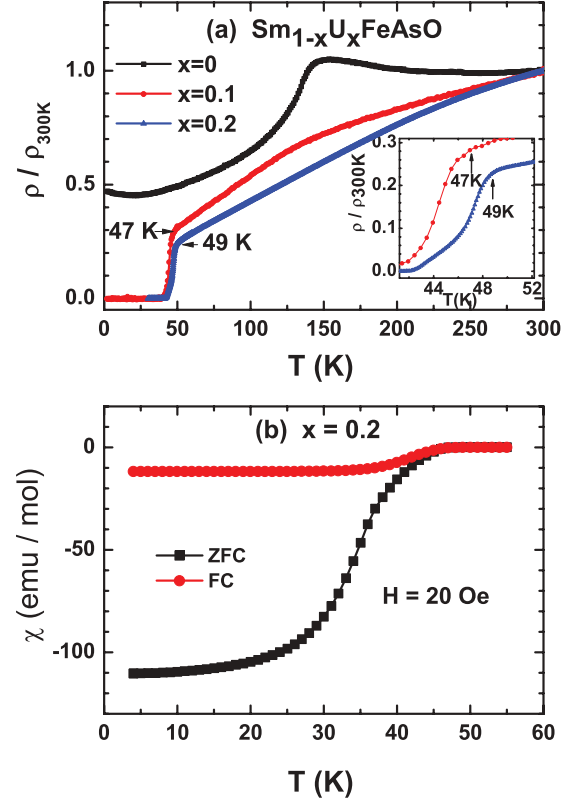


FIG. 2. (Color online) (a) Temperature dependence of resistivity for three $\text{Sm}_{1-x}\text{U}_x\text{FeAsO}$ samples in temperatures up to 300 K. (b) Temperature dependence of magnetic susceptibility of one U-doped sample with $x = 0.2$ in ZFC and FC situations under an applied field of 20 Oe.

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 (ZFC) and field-cooled (FC) 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.⁷⁻⁹

To obtain information about the 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 the $H \parallel ab$ plane.²⁶ 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 , $(dH_{c2}/dT)_{T=T_c} \approx -7.4$ T/K. This value is comparable to other 1111 systems with similar T_c .^{27,28} Then the simple

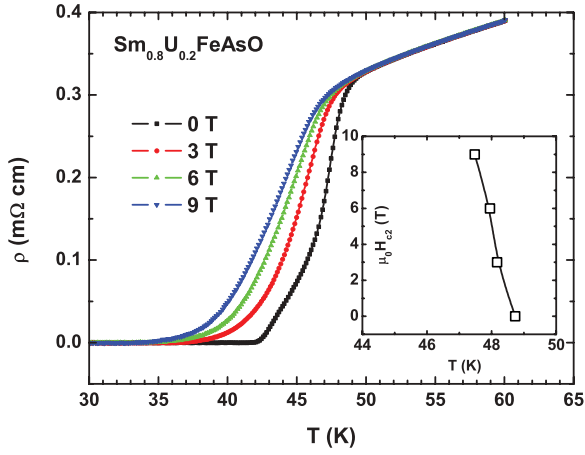


FIG. 3. (Color online) Temperature dependence of resistivity for the sample with $x = 0.2$ under different magnetic fields. The inset shows the phase diagram derived from the resistive transition curves taking a criterion of 95% ρ_n .

Werthamer-Helfand-Hohenberg (WHH) formula,²⁹ $H_{c2}(0) = -0.693T_c(dH_{c2}/dT)|_{T=T_c}$, is adopted to estimate the upper critical field to be 250 T.

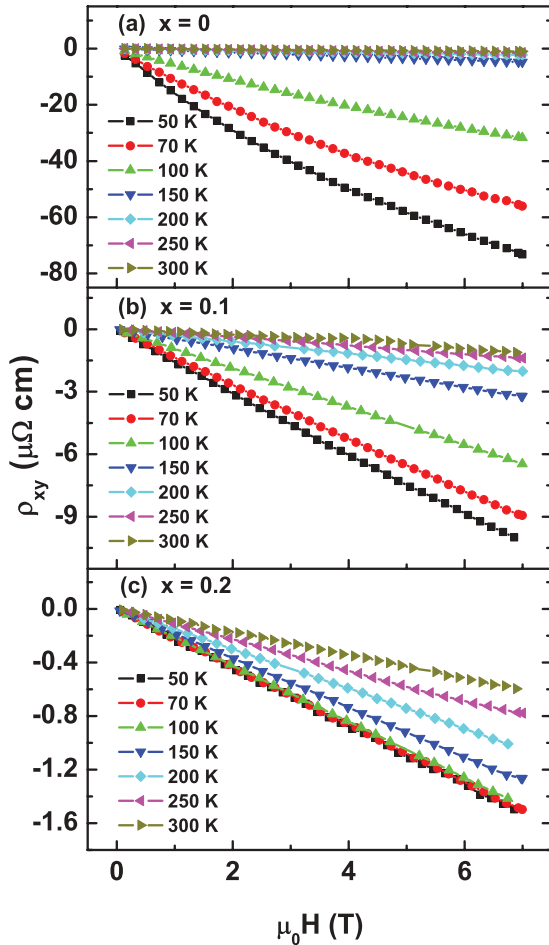


FIG. 4. (Color online) Field dependence of Hall resistivity ρ_{xy} in the normal state for three $\text{Sm}_{1-x}\text{U}_x\text{FeAsO}$ samples with $x = 0$ (a), 0.1 (b), and 0.2 (c).

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 ρ_{xy} at different temperatures for the samples with $x = 0, 0.1$, and 0.2 , respectively. The value of ρ_{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 ρ_{xy} is negative at all temperatures above the critical temperature, indicating the domination of electronlike charge carriers in the normal-state conduction. For the parent sample, however, the linear behavior can only be observed in temperatures above 150 K, suggesting a drastic change in the conducting conditions during the structural and antiferromagnetic transitions at 150 K.

The temperature dependence of the 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 the multiband effect in the present system.

In summary, we found that U doping is effective in inducing superconductivity in the 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 a 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 an approach to introduce superconductivity in the 1111 system, where the doping content is easier to control and

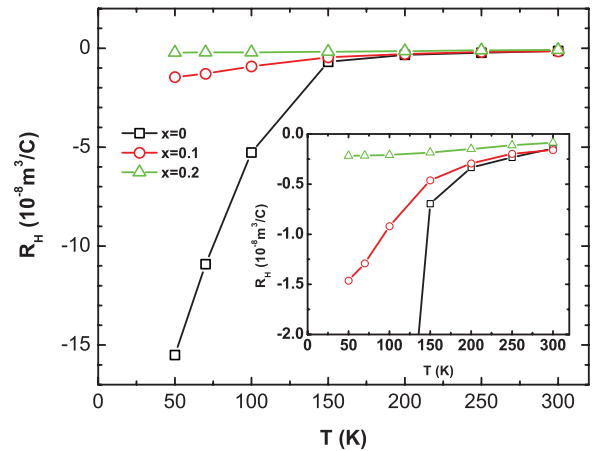


FIG. 5. (Color online) Temperature dependence of Hall coefficient R_H for the samples $\text{Sm}_{1-x}\text{U}_x\text{FeAsO}$ with $x = 0, 0.1$, and 0.2 . The inset shows the enlarged view of the same data.

the volume fraction of magnetic shielding is improved. The present system may be suitable for the single-crystal growth and in-depth research as the next step.

This work was supported by the National Natural Science Foundation of China (No. 91226108, No. 11274234, and No. 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).

*tangjun@scu.edu.cn

†mugang@mail.sim.ac.cn

- ¹Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, *J. Am. Chem. Soc.* **130**, 3296 (2008).
- ²G. 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).
- ³Z. 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).
- ⁴G. 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).
- ⁵X. H. Chen, T. Wu, G. Wu, R. H. Liu, H. Chen, and D. F. Fang, *Nature (London)* **453**, 761 (2008).
- ⁶P. 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).
- ⁷C. 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).
- ⁸L. 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).
- ⁹M. Xu, F. Chen, C. He, H. W. Ou, J. F. Zhao, and D. L. Feng, *Chem. Mater.* **20**, 7201 (2008).
- ¹⁰H. H. Wen, G. Mu, L. Fang, H. Yang, and X. Zhu, *Europhys. Lett.* **82**, 17009 (2008).
- ¹¹K. Kasperkiewicz, J. W. Bos, A. N. Fitch, K. Prassides, and S. Margadonna, *Chem. Commun.* 707 (2009).
- ¹²G. Mu, B. Zeng, X. Zhu, F. Han, P. Cheng, B. Shen, and H. H. Wen, *Phys. Rev. B* **79**, 104501 (2009).
- ¹³A. 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).
- ¹⁴C. 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).
- ¹⁵G. 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).
- ¹⁶Y. L. Chen, C. H. Cheng, Y. J. Cui, H. Zhang, Y. Zhang, Y. Yang, and Y. Zhao, *J. Am. Chem. Soc.* **131**, 10338 (2009).
- ¹⁷X. G. Ren, P. Rinke, and M. Scheffler, *Phys. Rev. B* **80**, 045402 (2009).
- ¹⁸C. 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).
- ¹⁹C. 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).
- ²⁰J. 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).
- ²¹R. H. Liu, G. Wu, T. Wu, D. F. Fang, H. Chen, S. Y. Li, K. Liu, Y. L. Xie, X. F. Wang, R. L. Yang, L. Ding, C. He, D. L. Feng, and X. H. Chen, *Phys. Rev. Lett.* **101**, 087001 (2008).
- ²²J. 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).
- ²³C. 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 (London)* **453**, 899 (2008).
- ²⁴Z. 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).
- ²⁵P. Cheng, H. Yang, Y. Jia, L. Fang, X. Y. Zhu, G. Mu, and H. H. Wen, *Phys. Rev. B* **78**, 134508 (2008).
- ²⁶X. Zhu, H. Yang, L. Fang, G. Mu, and H. H. Wen, *Supercond. Sci. Technol.* **21**, 105001 (2008).
- ²⁷Y. 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).
- ²⁸H. 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).
- ²⁹N. R. Werthamer, E. Helfand, and P. C. Hohenberg, *Phys. Rev.* **147**, 295 (1966).