PHYSICAL REVIEW B **83**, 212502 (2011)

Superconductivity and magnetic properties of single crystals of $K_{0.75}Fe_{1.66}Se_2$ and $Cs_{0.81}Fe_{1.61}Se_2$

J. J. Ying, X. F. Wang, X. G. Luo,[*] A. F. Wang, M. Zhang, Y. J. Yan, Z. J. Xiang, R. H. Liu, P. Cheng,
G. J. Ye, and X. H. Chen[†]

*Hefei National Laboratory for Physical Science at Microscale and Department of Physics, University of Science and Technology of China,
Hefei, Anhui 230026, People's Republic of China*

(Received 25 December 2010; revised manuscript received 10 April 2011; published 13 June 2011)

We successfully grew the high-quality single crystals of $A_xFe_2Se_2$ ($A =$ K and Cs) by self-flux method. Sharp superconducting transition was observed for both types of crystals. The crystals show the onset superconducting transition temperatures (T_c) of 31 and 30 K for K and Cs compounds, respectively, with nearly 100% superconductive shielding fraction. The crystals show quite high resistivity in the normal state of more than 160 and 1300 mΩ cm maximum resistivity for $K_xFe_2Se_2$ and $Cs_xFe_2Se_2$ single crystals, respectively. Much larger upper critical field H_{c2} is inferred from low-temperature isomagnetic-field magnetoresistance in these crystals than in FeSe. The anisotropy $H_{c2}^{ab}(0)/H_{c2}^{c}(0)$ is estimated to be around 3 for both of the two materials. Anisotropic peculiar magnetic behavior in normal state has been found for $Cs_xFe_2Se_2$

DOI: 10.1103/PhysRevB.83.212502 PACS number(s): 74.70.Xa, 74.10.+v, 74.25.F−, 74.25.Ha

The layered iron-pnictide compounds have attracted the intense interests since superconductivity at 26 K in ZrCuSiAs-type LaFeAs(O,F) (Ref. 1) was found. Replacing La with Sm leads to superconducting transition temperature $T_c = 43$ K (Ref. 2) and soon renewed to highest record ($T_c = 55$ K) (Refs. 3 and 4) in this type of compound. Up to now, various Fe-based superconductors, such as ZrCuSiAs-type LnFeAsO (Ln is rare earth elements),[1–3] $ThCr_2Si_2$-type $AeFe_2As_2$ (Ae is alkali earth elements),[5] Fe_2As-type AFeAs (A is Li or Na),[7–9] and anti-PbO-type Fe(Se,Te),[10] have been reported. The high T_c and superconductivity proximity to a magnetic ordering state,[6,11] which is thought to be similar to high-T_c superconductor cuprates, inspired worldwide passion of study toward elucidating the mechanism of high-T_c superconductivity. All of them have a common structural feature, that is, the edge-sharing $FeAs_4$ ($FeSe_4$) tetrahedra formed FeAs (FeSe) layers. The superconductivity in these compounds is thought to be intimately related to the height of anion from Fe layer.[12,13] Unlike the case of FeAs-based compounds, which usually possess cations between the FeAs layers, Fe(Se,Te) family has a extremely simple structure with only FeSe layers stacked along *c* axis without any intercalating cations.[10] The height of anion from Fe layer in Fe(Se,Te) can only be tuned by changing the relative proportion of Se and Te anions or by applying high pressure. T_c can reach 37 K (onset) under 4.5 GPa from the ambient 8 K in FeSe.[14] The corresponding pressure dependent ratio of T_c can reach as large as dT_c/dP of ∼9.1 K/GPa, which is the highest among all the Fe-based superconductors.[14–17] Taking into account the effect of local structure (such as, the height of the FeAs layer or the distance and the blocks between FeAs layers) on superconductivity in the FeAs-based compounds, superconductivity in Fe-Se family is expected to have a higher T_c at ambient pressure by intercalating cations between the FeSe layers. Very recently, by intercalating K, Rb, Cs, and Tl between the FeSe layers, superconductivity has been enhanced to about 30 K without any external pressure in Fe-Se system.[18–22] Although the highest T_c at ambient pressure for Fe-chalcogenides was achieved in K-intercalated FeSe, the superconducting fraction is low and the transition is broad. No full shielding fraction can be observed in Cs-intercalated FeSe samples either. Therefore, to investigate further intrinsic properties of intercalated FeSe compounds, single crystals with high quality, full superconductive shielding fraction, and sharp transition are required to grow in priority.

In this Brief Report, we successfully grew the single crystals of $K_xFe_2Se_2$ and $Cs_xFe_2Se_2$ with full superconductive shielding fraction by self-flux method. The crystals showed the onset T_c of 31 and 30 K for K and Cs compounds, respectively. Nearly 100% superconductive shielding fraction was observed through the zero-field-cooling (ZFC) magnetic susceptibility measurements. Since Fe-based high-T_c superconductors are thought to be closely related to magnetic interaction, the normal-state magnetization was also investigated.

Single crystals AFe_2Se_2 (A= K and Cs) were grown by self-flux method. Starting material FeSe was obtained by reacting Fe powder with Se powder with Fe:Se = 1:1 at 700 °C for 4 h. K and Cs pieces and FeSe powder were put into a small quartz tube with nominal composition as $K_{0.8}Fe_2Se_2$ and $Cs_{0.8}Fe_2Se_2$. Due to the high activity of K and Cs metals, the single wall quartz tube will be corrupted and broken during the growth procedure. Therefore, two-wall quartz tube is required. We realized it in the following way: the small quartz tube was sealed under high vacuum and then put in a bigger quartz tube followed by evacuating and being sealed. The mixture was heated to 1030 ° C in 4 h and then kept at this temperature for 2 h, and later slowly cooled down to 750 °C at a rate of 6 °C/h. After that, the temperature was cooled down to room temperature by shutting down the furnace. The obtained single crystals show a flat shiny surface with dark black color. The inset of Fig. 1(b) shows a piece of typical single crystal of $Cs_xFe_2Se_2$. K-compound crystals are easy to cleave and thin crystals with thickness less than 100 μm can be easily obtained, while Cs-compound crystals are fragile and quite difficult to cleave.

Single crystals of $K_xFe_2Se_2$ and $Cs_xFe_2Se_2$ were characterized by powder x-ray diffraction (XRD), inductively coupled plasma atomic emission spectroscopy (ICP-AES), x-ray single crystal diffraction, direct current (dc) magnetic susceptibility, and electrical transport measurements. Powder XRD and single crystal XRD were performed on TTRAX3 theta/2theta rotating anode x-ray diffractometer (Japan) with Cu Kα radiation and a fixed graphite monochromator. Magnetic susceptibility

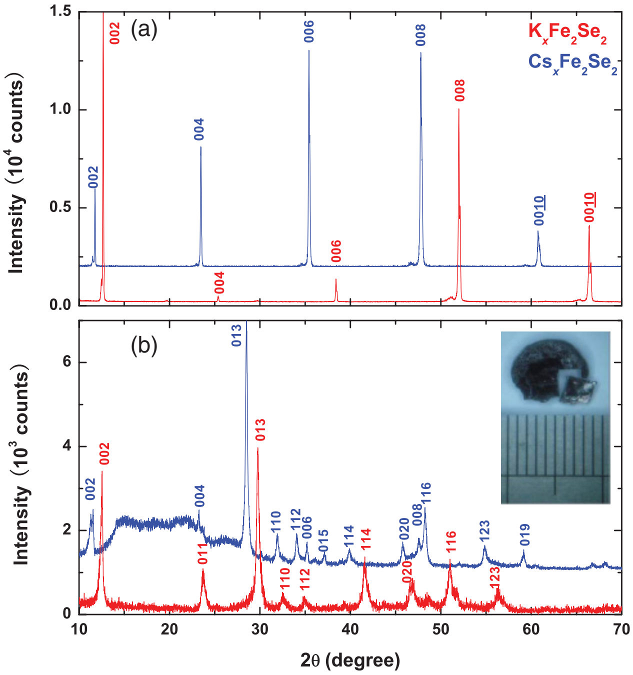

FIG. 1. (Color online) (a) The single crystal x-ray diffraction pattern of $K_xFe_2Se_2$ and $Cs_xFe_2Se_2$ (offset vertically for clarity); (b) x-ray diffraction pattern of the powdered $K_xFe_2Se_2$ and $Cs_xFe_2Se_2$ (offset vertically for clarity), all the peaks can be well indexed. The hump in XRD pattern for $Cs_xFe_2Se_2$ comes from the Mylar film, which has been used to protect the sample from air.

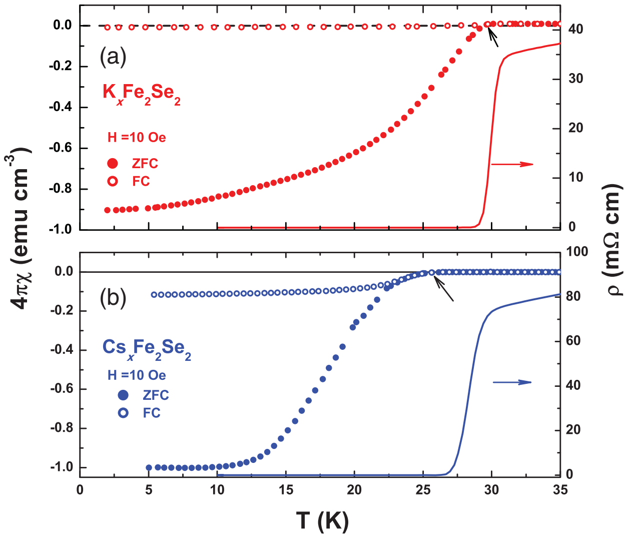

FIG. 2. (Color online) (a) The resistivity of $K_xFe_2Se_2$ around T_c (solid line), and its ZFC and FC susceptibility taken at 10 Oe with the magnetic field parallel to the *ab* plane. (b) The resistivity of $Cs_xFe_2Se_2$ around T_c (solid line), and its ZFC and FC susceptibility taken at 10 Oe with the magnetic field parallel to the *ab* plane.

was measured with the *Quantum Design* MPMS-SQUID. The measurement of resistivity and magnetoresistance were performed using the *Quantum Design* PPMS-9.

Figure 1 shows the x-ray single crystal diffraction and powder XRD after crushing the single crystals to powder for $K_xFe_2Se_2$ and $Cs_xFe_2Se_2$. Only $(00l)$ reflections were recognized in Fig. 1(a), indicating that both types of single crystals were perfectly oriented along c axis. The lattice parameters are obtained to index the powder XRD patterns in Fig. 1(b) with the symmetry of $I4/mmm$ and $a = 3.8912$ Å and $c = 14.1390$ Å for $K_xFe_2Se_2$. The lattice constant a obtained here is smaller than that in Refs. and 21. Small peaks can be found near the main $(00l)$ peaks, which should arise from the intrinsic inhomogeneous distribution of the intercalated alkali atoms.[23] The actual compositions of $K_xFe_2Se_2$ were determined by ICP-AES to be K:Fe:Se = 0.75:1.66:2, indicative of deficiencies on both K and Fe sites and consistent with the previous reports.[18,19] For $Cs_xFe_2Se_2$, the lattice parameters determined from the powder XRD patterns are $a = 3.9618$ Å and $c = 15.285$ Å, which is almost the same as that in Ref. 21. The actual composition of this crystal was determined by ICP-AES to be Cs:Fe:Se = 0.81:1.61:2, indicative of deficiencies on both Cs and Fe sites. This is consistent with previous reports.[20]

Figure 2(a) shows the resistivity and susceptibility measurements at low temperature for $K_xFe_2Se_2$. The resistivity starts to drop quickly at about 31 K and it reaches zero at about 28.7 K. The ZFC and field cooling (FC) susceptibilities show that the superconductive shielding begins to emerge at about 29 K with magnetic field parallel to the *ab* plane taken at 10 Oe. The superconductive shielding fraction estimated from the ZFC magnetization at 2 K is about 90%, which indicates the bulk superconductivity nature and good quality of the crystals. This superconductive shielding fraction is much larger than that in previous reports.[18–20] Figure 2(b) shows the low-temperature resistivity and susceptibility measurements for $Cs_xFe_2Se_2$. The onset transition temperature is about 30 K, and zero resistance is reached at 26.5 K. The superconductivity transition temperature taken from the ZFC and FC curves is estimated about 25.5 K. The superconductive shielding fraction estimated from the ZFC magnetization reaches 100% below 10 K estimated from the ZFC curve. It indicates a much better superconductivity than the crystals in the previous report.[20]

The temperature dependence of in-plane resistivity for the $K_xFe_2Se_2$ and $Cs_xFe_2Se_2$ from 10 to 300 K are shown in Fig. 3. The $K_xFe_2Se_2$ crystal shows the semiconducting behavior at the high temperature and displays a broad maximum at about 125 K. This temperature is slightly higher than that in the report by Guo *et al.* (around 100 K),[18] but much smaller than that reported by Mizuguchi *et al.* (∼200 K).[19] Also, the maximum resistivity in our sample (170 mΩ cm) is much smaller than that in previous report (∼3000 mΩ cm).[19] The different temperature and magnitude of the maximum resistivity could be related to the different deficiency of Fe or K. With further decreasing the temperature, the resistivity exhibits a metallic behavior and superconductivity emerges at about 30 K. The resistivity of $Cs_xFe_2Se_2$ shows a metallic behavior in the whole measuring temperature range, being quite different from that of the $K_xFe_2Se_2$. The resistivity of $K_xFe_2Se_2$ and $Cs_xFe_2Se_2$ are 70 and 1350 mΩ cm at room temperature, respectively, and all these values are much larger than those of FeSe single crystals[24] and the iron-pnictide superconductors.[25] This may arise from the strong scattering from large disorder induced by the Fe deficiencies.

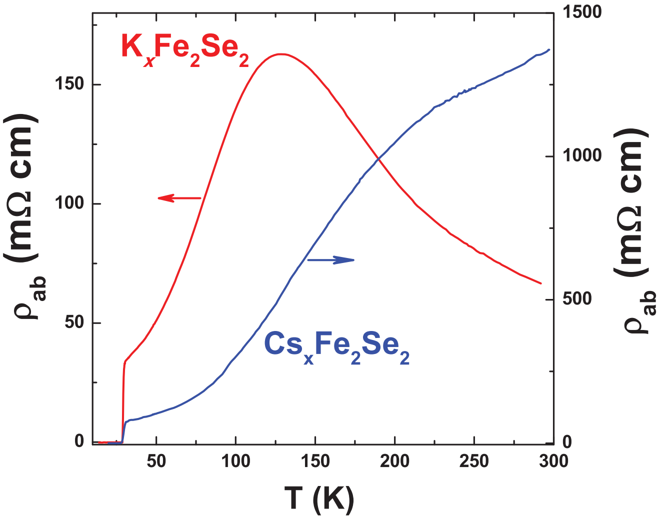

FIG. 3. (Color online) The temperature dependence of resistivity for $K_xFe_2Se_2$ and $Cs_xFe_2Se_2$.

The resistivity of $K_xFe_2Se_2$ and $Cs_xFe_2Se_2$ with different magnitude of magnetic field applied parallel and perpendicular to the *ab* plane around T_c are shown in Fig. 4(a)–4(d), respectively. The transition temperature of superconductivity is suppressed gradually and the transition is broadened with increasing magnetic field. We defined the T_c as the temperature where the resistivity was 90%, 50%, and 10% drop right above the superconducting transition. The anisotropy of the $H_{c2}(T)$ for $K_xFe_2Se_2$ and $Cs_xFe_2Se_2$ is shown in Fig. 4(e) and 4(f), respectively. Within the weak-coupling BCS theory, the upper critical field at $T = 0$ K can be determined by the Werthamer-Helfand-Hohenberg (WHH) equation[26] $H_{c2}(0) = 0.693[-(dH_{c2}/dT)]_{T_c}T_c$. Using the data of $H_{c2}(T)$ for the 90% resistivity drop, one obtains $[-(dH_{c2}^{ab}/dT)]_{T_c} = 9.86$ T/K, $[-(dH_{c2}^{c}/dT)]_{T_c} = 3.17$ T/K, and $T_c = 30.5$ K. The $H_{c2}(0)$ can be estimated to be 208 and 67 T with the field parallel and perpendicular to the *ab* plane for $K_xFe_2Se_2$, respectively. These values are a little larger than those in previous report.[19] For $Cs_xFe_2Se_2$ crystal, we have $[-(dH_{c2}^{ab}/dT)]_{T_c} = 6.21$ T/K, $[-(dH_{c2}^{c}/dT)]_{T_c} = 2.13$ T/K and $T_c = 29.3$ K. The $H_{c2}(0)$ is estimated to be 126 and 43 T with the field parallel and perpendicular to the *ab* plane, respectively. They are much smaller than those of $K_xFe_2Se_2$ although their T_cs are close to each other. We estimated the anisotropy $H_{c2}^{ab}(0)/H_{c2}^{c}(0)$ to be 3.1 and 2.9 for $K_xFe_2Se_2$ and $Cs_xFe_2Se_2$, respectively. This anisotropy value is larger than 1.70–1.86 in $Ba_{0.60}K_{0.40}Fe_2As_2$ (Ref. 27) and 1–2 in Fe(Se,Te) system,[28] but smaller than 4–6 in F-doped NdFeAsO.[29] Our results clearly indicate that the upper critical fields in the intercalated FeSe superconductors are higher than FeSe without any doubt.[10]

Figure 5 shows the magnetic susceptibility of $Cs_xFe_2Se_2$ with the magnetic field of 5 T applied parallel and perpendicular to the *c* axis. The magnetic susceptibility decreases gradually with decreasing the temperature at high temperature. The susceptibility starts to go upward at around 115 K with the field perpendicular to the *c* axis. While for the field parallel to the *c* axis, the susceptibility shows no upturn. The anomaly around 26 K is due to the transition of superconductivity. The decrease in susceptibility with temperature cooling down at high temperatures indicates there exists an antiferromagnetic coupling. Actually, recent neutron diffraction results indicate the spins aligned antiferromagnetically along the c axis below about 500 K.[30] The large value of susceptibility for field applied within the *ab* plane can be interpreted on the basis of such magnetic structure. Because of the strong strength of the antiferromagnetic alignment of the spins along *c* axis inferred

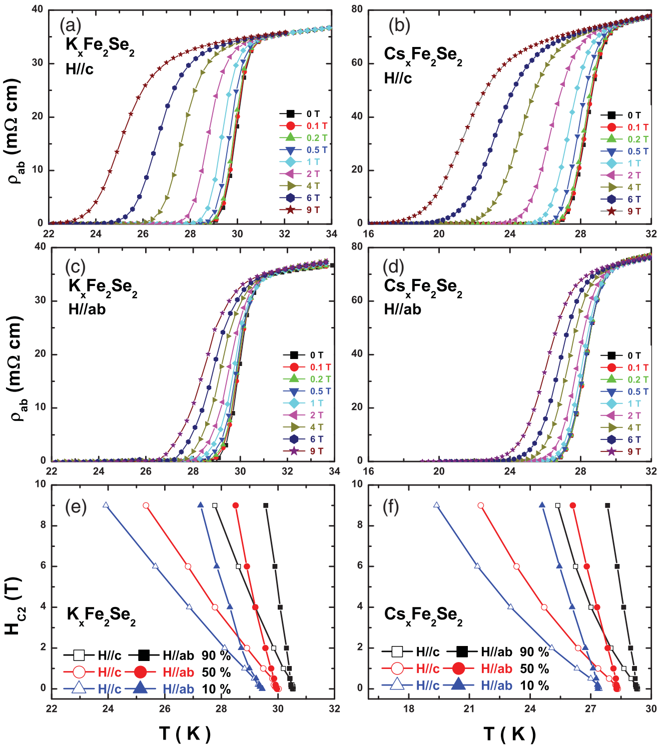

FIG. 4. (Color online) (a and c) The temperature dependence of resistivity for $K_xFe_2Se_2$ crystal with the magnetic field parallel and perpendicular to the *c* axis, respectively. (b and d) The temperature dependence of resistivity for $Cs_xFe_2Se_2$ crystal with the magnetic field parallel and perpendicular to the *c* axis, respectively. (e and f) The temperature dependence of $H_{c2}(T)$ for $K_xFe_2Se_2$ and $Cs_xFe_2Se_2$, respectively.

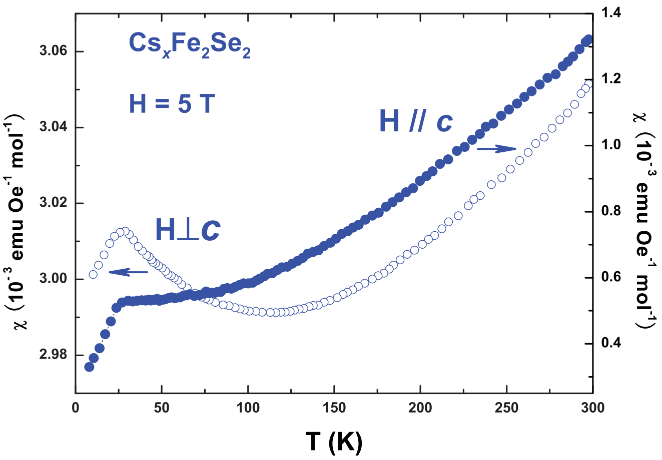

FIG. 5. (Color online) The magnetic susceptibility at 5 T for $Cs_xFe_2Se_2$ crystal with the magnetic field along and perpendicular to *c* axis.

from the very high transition temperature and large magnetic moment,[30] spins are easier to turn toward the direction of the magnetic field as field is applied within *ab* plane, which would surely induce the larger susceptibility. The occurrence of superconductivity could be related to such peculiar magnetic properties.

In summary, we successfully grew the single crystals of K- and Cs-intercalated FeSe compounds. T_c^{onset} is 31 and 30 K for $K_xFe_2Se_2$ and $Cs_xFe_2Se_2$, respectively. The ZFC dc magnetic susceptibility indicates that the superconductive shielding fraction is close to 100% for both types of crystals. The large H_{c2} observed in these materials is similar to the other iron-pnictide superconductors.[32] The anisotropy $H_{c2}^{ab}(0)/H_{c2}^{c}(0)$ is around 3 for both the two materials. The normal state resistivity is very large compared with the other iron-based superconductors. Such large resistivity could arise from the Fe vacancy in conducting FeSe layer.[30,32,33] Very high electrical resistance in these superconducting compounds could challenge the theoretical scenario for the mechanism of superconductivity. It should be addressed that their T_c is nearly the same although the resistivity behavior in $K_xFe_2Se_2$ and $Cs_xFe_2Se_2$ is quite different.

This work is supported by the Natural Science Foundation of China and by the Ministry of Science and Technology of China, and by Chinese Academy of Sciences.

---

*xgluo@mail.ustc.edu.cn

†chenxh@ustc.edu.cn

[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 **453**, 761 (2008).

[3] 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).

[4] R. 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, C. He, D. L. Feng, and X. H. Chen, Phys. Rev. Lett. **101**, 087001 (2008).

[5] H. Chen, Y. Ren, Y. Qiu, Wei Bao, R. H. Liu, G. Wu, T. Wu, Y. L. Xie, X. F. Wang, Q. Huang, and X. H. Chen, Europhys. Lett. **85**, 17006 (2009).

[6] D. R. Parker, M. J. Pitcher, P. J. Baker, I. Franke, T. Lancaster, S. J. Blundell, and S. J. Clarke, Chem. Commun. (Cambridge) , **2009**, 2189.

[7] F. C. Hsu, J. Y. Luo, K. W. The, T. K. Chen, T. W. Huang, P. M. Wu, Y. C. Lee, Y. L. Huang, Y. Y. Chu, D. C. Yan, and M. K. Wu, Proc. Natl. Acad. Sci. USA **105**, 14262 (2008).

[8] 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, Solid State Commun. **148**, 538 (2008).

[9] 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).

[10] Y. Mizuguchi, Y. Hara, K. Deguchi, S. Tsuda, T. Yamaguchi, K. Takeda, H. Kotegawa, H. Tou, and Y. Takano, Supercond. Sci. Technol. **23**, 054013 (2010).

[11] J. H. Tapp, Z. Tang, B. Lv, K. Sasmal, B. Lorenz, Paul C. W. Chu, and A. M. Guloy, Phys. Rev. B **78**, 060505(R) (2008).

[12] H. Okabe, N. Takeshita, K. Horigane, T. Muranaka, and J. Akimitsu, Phys. Rev. B **81**, 205119 (2010).

[13] S. Medvedev, T. M. McQueen, I. Trojan, T. Palasyuk, M. I. Eremets, R. J. Cava, S. Naghavi, F. Casper, V. Ksenofontov, G. Wortmann, and C. Felser, Nat. Mater.**8**, 630 (2009).

[14] Y. Mizuguchi, F. Tomioka, S. Tsuda, T. Yamaguchi, and Y. Takano, Appl. Phys. Lett. **93**, 152505 (2008).

[15] S. Margadonna, Y. Takabayashi, Y. Ohishi, Y. Mizuguchi, Y. Takano, T. Kagayama, T. Nakagawa, M. Takata, and K. Prassides, Phys. Rev. B **80**, 064506 (2009).

[16] G. Garbarino, A. Sow, P. Lejay, A. Sulpice, P. Toulemonde, M. Mezouar, and M. Nunez-Regueiro, Europhys. Lett. **86**, 27001 (2009).

[17] J. Guo, S. Jin, G. Wang, S. Wang, K. Zhu, T. Zhou, M. He, and X. Chen, Phys. Rev. B **82**, 180520 (2010).

[18] Y. Mizuguchi, H. Takeya, Y. Kawasaki, T. Ozaki, S. Tsuda, T. Yamaguchi, and Y. Takano, Appl. Phys. Lett. **98**, 042511 (2011).

[19] A. Krzton-Maziopa, Z. Shermadini, E. Pomjakushina, V. Pomjakushin, M. Bendele, A. Amato, R. Khasanov, H. Luetkens, and K. Conder, J. Phys. Condens. Matter **23**, 052203 (2011).

[20] A. F. Wang, J. J. Ying, Y. J. Yan, R. H. Liu, X. G. Luo, Z. Y. Li, X. F. Wang, M. Zhang, G. J. Ye, P. Cheng, Z. J. Xiang, and X. H. Chen, Phys. Rev. B **83**, 060512(R) (2011).

[21] M. Fang, H. Wang, C. Dong, Z. Li, C. Feng, J. Chen, and H. Q. Yuan, Europhys. Lett. **94**, 27009 (2011).

[22] X. G. Luo, X. F. Wang, J. J. Ying, Y. J. Yan, Z. Y. Li, M. Zhang, A. F. Wang, P. Cheng, Z. J. Xiang, G. J. Ye, R. H. Liu, and X. H. Chen, New J. Phys. **13**, 053011 (2011).

[23] D. Braithwaite, B. Salce, G. Lapertot, F. Bourdarot, C. Marin, D. Aoki, and M. Hanfland, J. Phys. Condens. Matter **21**, 232202 (2009).

[24] X. F. Wang, T. Wu, G. Wu, R. H. Liu, H. Chen, Y. L. Xie, and X. H. Chen, New J. Phys. **11**, 045003 (2009).

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

[26] Z. S. Wang, H.-Q. Luo, C. Ren, and H.-h. Wen, Phys. Rev. B **78**, 140501(R) (2008).

[27] M. Fang, J. Yang, F. F. Balakirev, Y. Kohama, J. Singleton, B. Qian, Z. Q. Mao, H. Wang, and H. Q. Yuan, Phys. Rev. B **81**, 020509(R) (2010).

[28] Y. Jia, P. Cheng, L. Fang, H. Luo, H. Yang, C. Ren, L. Shan, C. Gu, and H.-H. Wen, Appl. Phys. Lett. **93**, 032503 (2008).

[29] W. Bao, Q. Huang, G. F. Chen, M. A. Green, D. M. Wang, J. B. He, X. Q. Wang, and Y. Qiu, arXiv:1102.0830 (unpublished).

[30] H. Q. Yuan, J. Singleton, F. F. Balakirev, S. A. Baily, G. F. Chen, J. L. Luo, and N. L. Wang, Nature **457**, 565 (2009).

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

[32] V. Yu. Pomjakushin, E. V. Pomjakushina, A. Krzton-Maziopa, K. Conder, and Z. Shermadini, J. Phys. Condens. Matter **23**, 156003 (2011).

[33] Z. Wang, Y. J. Song, H. L. Shi, Z. W. Wang, Z. Chen, H. F. Tian, G. F. Chen, J. G. Guo, H. X. Yang, and J. Q. Li, Phys. Rev. B **83**, 140505(R) (2011).