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Transport critical currents in the iron pnictide superconducting wires prepared by the *ex situ* PIT method

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Abstract
The discovery of iron-based superconductors, the first non-cuprate family of superconductors with T_c above 40 K, has stimulated enormous interest in the field of superconductivity since last year. This remarkable discovery not only offers the opportunity to study the origin of superconductivity, but also opens up new possibilities of application. One of the most fascinating and useful properties of superconductors is the ability to carry electrical current with zero resistance. Here, we report the successful fabrication of dense $Sr_{0.6}K_{0.4}Fe_2As_2$ superconducting wires using the *ex situ* powder-in-tube (PIT) method and demonstrate a transport J_c of 3750 A cm^{-2} at 4.2 K. The connectivity of grains was improved upon doping (Ag or Pb) and the transport property of $Sr_{0.6}K_{0.4}Fe_2As_2$ wires was enhanced for a lead-doped sample, especially in low fields, to a best I_c of 37.5 A. Our results suggest that grain boundary properties require much greater attention when looking for applications of the high-T_c iron-based superconductors.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

It is known that superconductors, especially high-T_c superconductors, have great potential application in magnetic resonance imaging, magnets, particle accelerators and fusion reactors. However, what is really needed is a high-T_c round-shape wire. Up to now, two classes of materials with higher critical temperature, copper-oxide-based and MgB_2, have been systemically studied as superconducting current-carrying conductor. However, practical applications of these materials have been hampered by two major difficulties: grain boundaries and flux pinning. In order to improve the poor J_c tolerance against high magnetic fields, special techniques, such as sophisticated crystallographic texture fabrication and the introduction of flux pinning centers by irradiation or doping, must be performed, which undoubtedly adds complexity and delays applications. The recently discovered iron-based superconductors offer a new opportunity for application [1]. To date, four homologous series of Fe-based superconductors have been identified, commonly denoted as the 1111 phase (REFeAsO with RE = rare earth) [2–6], 122 phase ($AEFe_2As_2$ with AE = alkaline earth) [7–9], 111 phase (AFeAs with A = alkali metal) [10] and 11 phase (FeTe or FeSe) [11]. Among these, the 122 family is more advantageous compared with the other three classes of material: with nearly isotropic ($\gamma < 2$) and strong vortex pinning. In addition, moderate critical temperatures and high upper critical fields make the 122 compounds very attractive candidates for superconducting wires. Recently we reported the fabrication of niobium-clad $Sr_{0.6}K_{0.4}Fe_2As_2$ wires [12]; unfortunately no significant transport critical current was measured. In this paper, we present $Sr_{0.6}K_{0.4}Fe_2As_2$ superconducting wires fabricated by the *ex situ* powder-in-tube (PIT) method using $Sr_{0.6}K_{0.4}Fe_2As_2$ powder and Ag as a sheath material. Large transport critical currents were achieved. Our results indicate that the critical current density J_c can be strongly enhanced upon chemical addition, showing a best value for J_c of ~3750 A cm^{-2}

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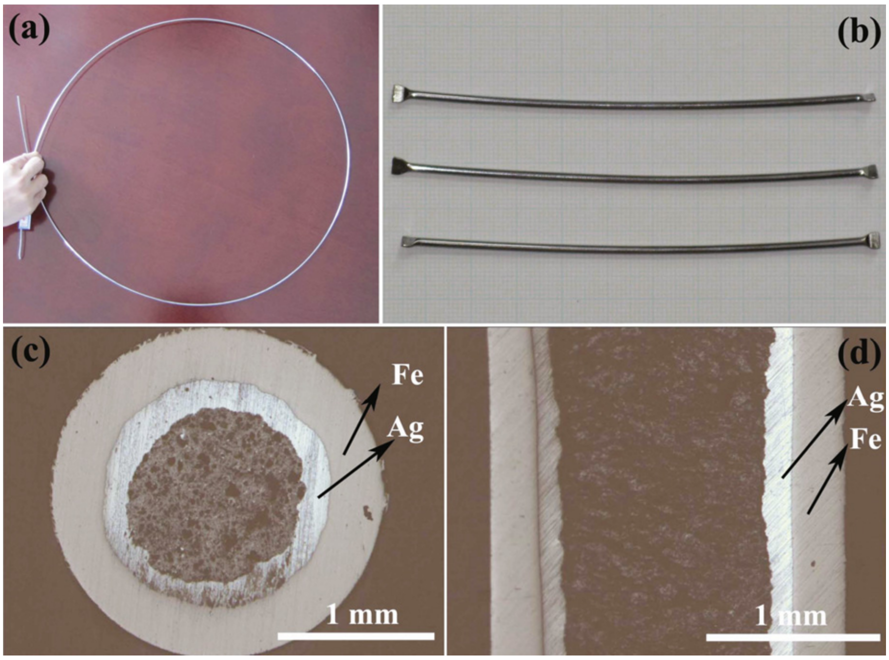

Figure 1. $Sr_{0.6}K_{0.4}Fe_2As_2$ wires fabricated by the *ex situ* PIT method. (a) Photograph of obtained wire, diameter 2.1 mm, showing its flexibility; (b) samples after cutting and before heating; (c) typical transverse and (d) longitudinal cross-sections of the $Sr_{0.6}K_{0.4}Fe_2As_2$ wires after heat treatment.

(I_c = 37.5 A) at 4.2 K, obtained for Pb-doped wires, the highest value in iron-based wires and tapes reported so far.

2. Experimental details

The $Sr_{0.6}K_{0.4}Fe_2As_2$ composite wires were prepared with the *ex situ* powder-in-tube (PIT) technique where bimetallic silver/iron tubes were used. The raw materials (Sr filings, Fe powder, As and K pieces), were accurately weighed according to the stoichiometric ratio of $Sr_{0.6}K_{0.4}Fe_2As_2$, then thoroughly ground in an Ar atmosphere for more than 5 h using a ball milling method. The powder was packed into a Nb tube; after packing, this tube was then heated to 850 °C and kept at this temperature for 35 h. The samples were reground and packed into a bimetallic tube of 10 mm outside diameter and 2 mm wall thickness. After packing, the tube was rotary swaged and then drawn to wires of 2 mm in diameter. The wires were cut into 8–10 cm lengths. They were then annealed at 900 °C for 20 h. It is noted that the grinding and packing processes were carried out in glove box filled with a high purity argon atmosphere. In order to investigate the effect of doping on critical currents, metallic silver or lead powder (10 wt%, 200 mesh, 99.9% purity) was doped in the samples, and then prepared with the same method.

The phase identification and crystal structure investigation were carried out using x-ray diffraction (XRD) with Cu Kα radiation at 20°–80° 2θ. The diffraction peaks could be well indexed on the basis of tetragonal $ThCr_2Si_2$-type structure with the space group $I4/mmm$, but some impurity phases are also detected, which were attributed to unreacted material or unstable behavior of $Sr_{0.6}K_{0.4}Fe_2As_2$. The microstructure was studied using scanning electron microscopy (SEM) after peeling away the sheath. The resistance measurements were done by a standard four-probe technique in a range of magnetic fields, using a physical property measurement system (PPMS). The DC magnetization measurements were done with a superconducting quantum interference device (SQUID). The transport critical current at 4.2 K and its magnetic dependence were evaluated at the High Field Laboratory for Superconducting Materials (HFLSM) in Sendai. The I_c measurement was performed for 3–5 samples to check reproducibility.

3. Results and discussion

Figure 1(a) shows a photograph of the obtained wire, which is nearly 1 m in length. The wire was cut into pieces 8–10 cm in length before sintering (figure 1(b)). Cross-and longitudinal-section photomicrographs of a typical wire after heat treatment are shown in figures 1(c), (d). The diameter of the superconducting core is 1.1 mm. It is evident that the $Sr_{0.6}K_{0.4}Fe_2As_2$ core presents a homogeneous cross-section with no reaction layer between the superconducting core and the bimetallic sheath. EDX line scan also confirmed the clear interface. The use of proper diffusion barrier metals has been found to be critical. We found that most metals, including Fe, Nb and Ta, can react with the iron-based compound at moderate to high temperatures and degrade the superconducting properties [12–14]. Our present results indicate that Ag is benign at high temperatures when in proximity to the compound, so silver is a very attractive metal component for FeAs-122 type superconducting wires.

Figure 2 shows the superconducting properties of $Sr_{0.6}K_{0.4}Fe_2As_2$ wires. Samples show a sharp drop in resistance at 35 K (figure 2(a)), with a width $\Delta T = 1$ K, which is close to the 37 K reported in the bulk superconductor [8].

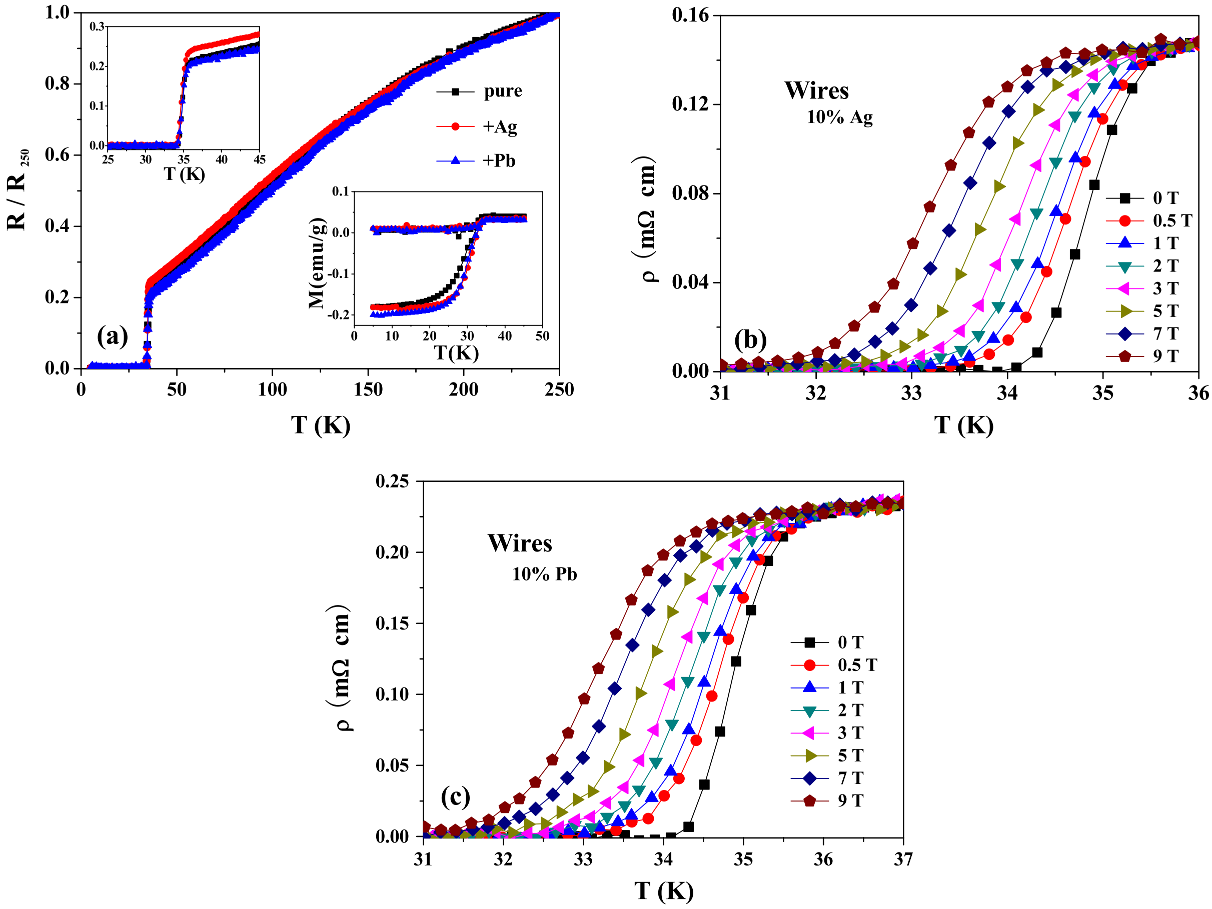

Figure 2. Superconducting properties of $Sr_{0.6}K_{0.4}Fe_2As_2$ wire. (a) Temperature dependence of the resistivity. The insets show an enlarged view of low temperature (top) and the temperature dependence of the DC magnetization (bottom). (b) Resistivity at different fields of Ag-doped $Sr_{0.6}K_{0.4}Fe_2As_2$ wire. (c) Resistivity at different fields of Pb-doped $Sr_{0.6}K_{0.4}Fe_2As_2$ wire.

The value of the critical transition temperature T_c is almost the same between pure and doped wires. The diamagnetic transitions of the samples are shown in the lower inset of figure 2(a), measured by the zero-field-cooled (ZFC) and field-cooled (FC) processes under a DC magnetic field of 10 Oe. The diamagnetism, consistent with the R–T data, confirms the bulk superconductivity in our samples. Figures 2(b)–(c) show the temperature dependence of the resistivity at various magnetic fields for the 10 wt% Ag- and Pb- doped wires. With increasing magnetic fields, the superconducting transitions are shifted to lower temperatures and become slightly broadened for both doped compounds. It should be noted that a similar phenomenon has been observed in the bulk samples [8]. We have estimated the upper critical field (H_{c2}) and the irreversibility field (H_{irr}), using the 90% and 10% values of the resistive transition curves. A rough estimation of the upper critical field at zero field gives a value higher than 150 T by using the Werthamer–Helfand–Hohenberg formula $H_{c2}(0) = 0.693 \times (dH_{c2}/dT) \times T_c$ [15], which is consistent with values obtained for bulk samples [8]. Note that similar H_{c2} and H_{irr} were obtained in pure and doped samples.

Figure 3 shows the transport critical current properties of $Sr_{0.6}K_{0.4}Fe_2As_2$ wires, measured at 4.2 K by a standard four-point method. It should be noted that zero-resistance currents

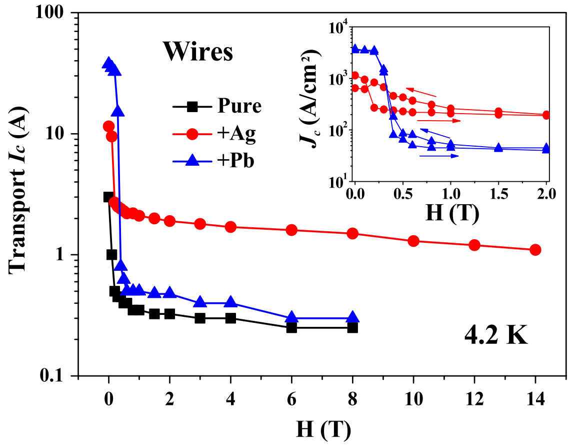

Figure 3. Transport I_c properties of $Sr_{0.6}K_{0.4}Fe_2As_2$ wires. The inset shows its transport critical current density J_c, measured under increasing and decreasing fields (notice the hysteretic phenomenon).

on the current–voltage curves were clearly seen for all Ag sheathed wires; by contrast, we did not observe significant transport critical currents in Nb or Ta sheathed iron-based wires [12], which may be related to bad grain connectivity as well as the reaction layer between the sheath and the superconducting core. The critical current values of short

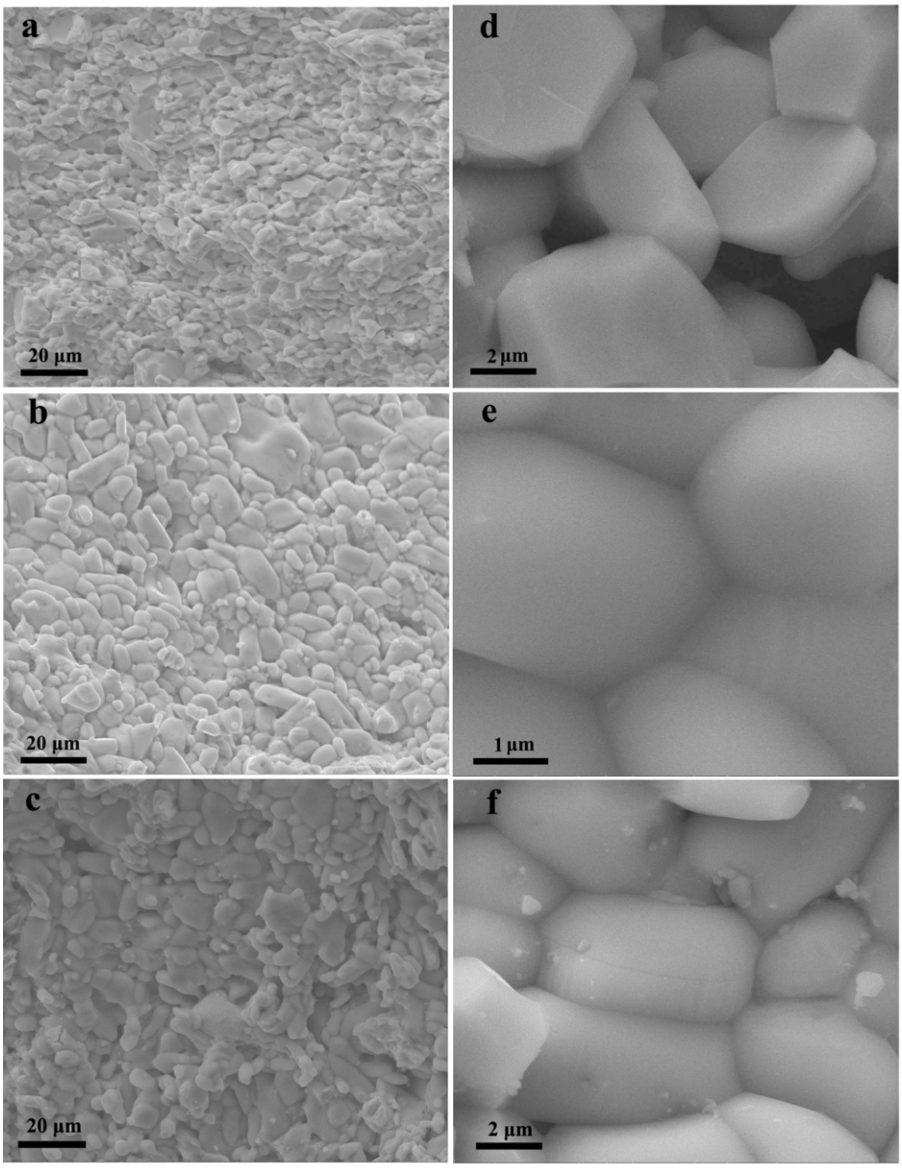

Figure 4. SEM micrographs of superconducting cores of the pure ((a), (d)), Ag-doped ((b), (e)) and Pb-doped ((c), (f)) wires.

pieces of the pure wire were ∼4 A in zero field, using a criterion of 1 μV cm^{-1}.

We have found that the critical current was strongly improved by Ag doping, increasing from 4 A for the pure sample to 11.5 A for the doped sample in zero field, and more important a super-current of 1 A still flowed in the wire even under a field as high as 14 T. The I_c is almost field independent between 0.2 and 10 T. Furthermore, it is remarkable that I_c reached values as high as 37.5 A in zero field for the Pb-doped sample, a factor of ∼12 higher than that of the pure samples. The critical current density J_c, calculated using a core cross-section of 1.0 mm^2, is shown in the inset of figure 3. As expected, a critical current density J_c, up to ∼3750 A cm^{-2} at 0 T, was achieved, which is comparable to the intragrain J_c of RE-1111 (RE: rare earth) estimated from magnetic data. Our present results clearly demonstrated that the transport J_c values of $Sr_{0.6}K_{0.4}Fe_2As_2$ wires can be significantly enhanced by doping, especially in low fields.

The field dependence of J_c in an increasing as well as a decreasing field was also characterized, and an apparent history effect was observed. A representative hysteretic J_c curve for a wire sample is shown in the inset of figure 3(a). This behavior has been also observed in some other superconductors [16, 17]. The hysteretic effects are supposed to be related to penetration of flux into strong pinning intragranular regions, and that the presence of intragranular critical currents enhances intergranular critical currents when the applied field is reduced from higher values [18]. The steep drop of J_c at low fields and the hysteretic curve J_c (inset of figure 3) relate to weak-link characteristics, as observed in the cuprate high-temperature superconductors, also consistent with the case of $Ba(Fe_{1-x}Co_x)_2As_2$ [19].

In order to investigate the reason for the J_c improvement, we studied the difference in microstructures of both pure and doped wires. Figure 4 presents scanning microscopy photomicrographs. Well-developed grains can be seen in all three samples, however, there are large differences between the pure and doped samples (figures 4(d)–(f)): the pure sample shows non-agglomerate grains, with sharp corners, like brick stacks huddled randomly (figure 4(d)). In contrast, the Ag-doped sample shows a dense microstructure, the improvement of the grain boundaries seems to occur during thermal treatment thanks to the chemical addition (figure 4(e)). We think that Ag mineralizes at the grain boundaries, thereby decreasing the melting temperature and improving the grain connectivity. In other words, addition acts as a sintering aid to eliminate cracks and voids, adding more free channels between dislocations at grain boundaries. Similar phenomena could be found in Pb-doped samples: most of grains seem to partially melt (figure 4(f)), resulting in a better connectivity.

The early experimental results indicate that the bulk critical current is limited by intergrain currents over the grain boundaries in polycrystalline samples [19–21]. Similar to the d-wave cuprates, grain boundary crystalline disorder depresses the superconducting transport properties in iron pnictide superconductors; therefore, it is necessary to improve the intergrain connection in iron-based superconductors. Recently it has been reported that the superconducting properties of bulk $Sr_{1-x}K_xFe_2As_2$ samples can be improved upon silver doping [22]. We now add chemical addition into $Sr_{0.6}K_{0.4}Fe_2As_2$ wires to improve transport properties. As mentioned above, all doped samples show a higher J_c than pure samples in the low field region. However, there is a large difference between Ag- and Pb-doped samples: upon Ag doping, the value of J_c is increased in the entire field region, especially at high fields, meanwhile, in the Pb doping case, a significant enhancement can be achieved only at 0 T. From the above J_c and SEM results discussed, it can be concluded that Ag or Pb helps in enhancing the critical current density in the superconducting wires by eliminating cracks and improving grain connection. In other words, the transport properties of $Sr_{1-x}K_xFe_2As_2$ wires have been improved by chemical addition; however, the reason for different doping effects is unknown so far and further investigations are needed to clarify what occurs at the grain boundaries.

4. Conclusions

In summary, large transport J_c values were obtained in $Sr_{0.6}K_{0.4}Fe_2As_2$ wires, a factor of $\sim$37 higher than the value obtained in Fe–Se–Te wires [23]. However, the process control is far from optimized and it is believed that further improvement in the transport capability of iron-based superconducting wires is possible upon either the achievement of minimizing secondary phases, or enhancing the packing density in the sample. On the other hand, the particles (Ag or Pb) incorporated into the system by addition will remain between the grains, producing a substantial effect on the grain growth and grain connectivity, thus the transport properties of $Sr_{0.6}K_{0.4}Fe_2As_2$ wires can be enhanced upon doping. Given how deleterious current-blocking effects have been to applications of the cuprates, it is indeed very important to understand the properties of the grain boundary in much greater detail in iron-based superconductors and in the quest for new special processes to eliminate the current-blocking effect.

Acknowledgments

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References

[1] Kamihara Y, Watanabe T, Hirano M and Hosono H 2008 *J. Am. Chem. Soc.* **130** 3296
[2] Chen X-H, Wu T, Wu G, Liu R-H, Chen H and Fang D-F 2008 *Nature* **453** 376
[3] Chen G-F, Li Z, Wu D, Li G, Hu W-Z, Dong J, Zheng P, Luo J-L and Wang N-L 2008 *Phys. Rev. Lett.* **100** 247002
[4] Ren Z-A *et al* 2008 *Europhys. Lett.* **82** 57002
[5] Wen H-H, Mu G, Fang L, Yang H and Zhu X 2008 *Europhys. Lett.* **82** 17009
[6] Ma Y-W, Gao Z-S, Wang L, Qi Y-P, Wang D-L and Zhang X-P 2009 *Chin. Phys. Lett.* **26** 037401
[7] Rotter M, Tegel M and Johrendt D 2008 *Phys. Rev. Lett.* **101** 107006
[8] Sasmal K, Lv B, Lorenz B, Guloy A, Chen F, Xue Y and Chu C W 2008 *Phys. Rev. Lett.* **101** 107007
[9] Qi Y-P, Gao Z-S, Wang L, Wang D-L, Zhang X-P and Ma Y-W 2008 *New J. Phys.* **10** 123003
[10] Wang X-C, Liu Q-Q, Lv Y-X, Gao W-B, Yang L-X, Yu R-C, Li F-Y and Jin C-Q 2008 *Solid State Commun.* **148** 538
[11] Hsu F-C *et al* 2008 *Proc. Natl Acad. Sci. USA* **105** 14262
[12] Qi Y-P, Zhang X-P, Gao Z-S, Zhang Z-Y, Wang L, Wang D-L and Ma Y-W 2009 *Physica* C **469** 717
[13] Gao Z-S, Wang L, Qi Y-P, Wang D-L, Zhang X-P and Ma Y-W 2008 *Supercond. Sci. Technol.* **21** 105024
[14] Gao Z-S, Wang L, Qi Y-P, Wang D-L, Zhang X-P and Ma Y-W 2008 *Supercond. Sci. Technol.* **21** 112001
[15] Werthamer N R, Helfand E and Hohenberg P C 1966 *Phys. Rev.* **147** 295–302
[16] Matsushita T, Ni B, Yamafuji K, Watanabe K, Noto K, Morita H, Fujimori H and Muto Y 1989 *Advances in Superconductivity* ed K Kitazawa and T Ishiguro (Tokyo: Springer-Verlag) pp 393–7
[17] Watanabe K, Noto K, Morita H, Fujimori H, Mizuno K, Aomine T, Ni B, Matsushita T, Yamafuji K and Muto Y 1989 *Cryogenics* **29** 263
[18] Mchenry M E 1989 *Phys. Rev.* B **40** 2666
[19] Lee S *et al* 2009 *Appl. Phys. Lett.* **95** 212505
[20] Kametani F *et al* 2009 *Appl. Phys. Lett.* **95** 142502
[21] Yamamoto A *et al* 2008 *Supercond. Sci. Technol.* **21** 095008
[22] Wang L, Qi Y-P, Gao Z-S, Wang D-L, Zhang X-P and Ma Y-W 2010 *Supercond. Sci. Technol.* **23** 025027
[23] Mizuguchi Y, Deguchi K, Tsuda S, Yamaguchi T, Takeya H, Kumakura H and Takano Y 2009 *Appl. Phys. Express* **2** 083004