Pressure effect on superconductivity of $A_x\text{Fe}_2\text{Se}_2$ ($A = \text{K and Cs}$)
Pressure effect on superconductivity of $A_x\text{Fe}_2\text{Se}_2$ ($A = \text{K and Cs}$)

J J Ying, X F Wang, X G Luo, Z Y Li, Y J Yan, M Zhang, A F Wang, P Cheng, G J Ye, Z J Xiang, R H Liu 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
E-mail: chenxh@ustc.edu.cn

New Journal of Physics 13 (2011) 033008 (9pp)
Received 7 January 2011
Published 8 March 2011
Online at http://www.njp.org/
doi:10.1088/1367-2630/13/3/033008

Abstract. We have performed high hydrostatic pressure resistivity measurements (up to 1.7 GPa) on the newly discovered superconductor $A_x\text{Fe}_2\text{Se}_2$ ($A = \text{K and Cs}$) single crystals. Two batches of single crystals $K_x\text{Fe}_2\text{Se}_2$ with different transition temperatures ($T_c$) were used to study the effect of pressure. The $T_c$ of the first one gradually decreases with increasing pressure from 32.6 K at ambient pressure. While a dome-like behavior was observed for the crystal with $T_c = 31.1$ K, $T_c$ reaches its maximum value of 32.7 K at the pressure of 0.48 GPa. This indicates that there exists an optimal doping with maximum $T_c$ of 32.7 K in the $K_x\text{Fe}_2\text{Se}_2$ system. The behavior of $T_c$ versus pressure for $Cs_x\text{Fe}_2\text{Se}_2$ also shows a dome-like behavior, and $T_c$ reaches its maximum value of 31.1 K at a pressure of 0.82 GPa. The hump observed in the temperature dependence of resistivity for all of the samples tends to shift to high temperature with increasing pressure. The resistivity hump could arise from the vacancy of Fe or Se.
The newly discovered iron-based superconductors have attracted much attention over the last three years [1]–[5]. Until now, various Fe-based superconductors, such as ZrCuSiAs-type \( LnFeAsO \) (\( Ln \) stands for rare earth elements) [1]–[3], ThCr\(_2\)Si\(_2\)-type \( AFe_2As_2 \) (\( A \) stands for alkali earth elements) [5], Fe\(_2\)As-type \( AFeAs \) (\( A \) is Li or Na) [6]–[8] and anti-PbO-type Fe(Se, Te) [9], have been reported. The transition temperature \( T_c \) of anti-PbO-type FeSe could reach 37 K under 4.5 GPa from \( T_c \sim 8 \) K at ambient pressure [10, 11, 13, 31]. Very recently, by intercalating K, Rb, Cs and Tl in between the FeSe layers, superconductivity was enhanced to about 30 K without any external pressure in the Fe–Se system [14]–[19], and it provides a new type of iron-based superconductor to explore high \( T_c \). For the iron-pnictide, the pressure tends to destroy the magnetic transition in the undoped compounds, and \( T_c \) increases with increasing pressure for underdoped iron-pnictides, remaining approximately constant for optimal doping and decreasing linearly in the overdoped range [20, 21]. Superconductivity can be induced via pressure in the parent compounds \( AFe_2As_2 \) (\( A = Ca, Sr, Ba, Eu \)) [22]–[24]. Magnetism and superconductivity are strongly correlated with each other in iron-based superconductors. The strong pressure effect in FeSe may be related to its strongly enhanced antiferromagnetic spin fluctuations under pressure [25]. Therefore, we wonder whether the strong pressure effect still exists in \( A_xFe_2Se_2 \). It is very meaningful to carry out high-pressure measurements in these newly found superconductors.

In this paper, we systematically measured resistivity under high hydrostatic pressure up to 1.7 GPa for the newly discovered superconductors \( K_xFe_2Se_2 \) and \( Cs_xFe_2Se_2 \). It is found that the transition temperature slightly increases below 0.82 GPa and gradually decreases with further increasing the pressure for \( Cs_xFe_2Se_2 \). Two \( K_xFe_2Se_2 \) single crystals with different \( T_c \) were measured. For the \( K_xFe_2Se_2 \) crystal with \( T_c^{onset} = 32.6 \) K and a broad hump centered at 245 K, \( T_c \) gradually decreases with increasing pressure. While \( T_c \) versus pressure shows similar behavior to \( Cs_xFe_2Se_2 \), \( T_c^{onset} \) reaches its maximum value of 32.7 K under the pressure of 0.48 GPa for the \( K_xFe_2Se_2 \) with \( T_c^{onset} = 31.1 \) K and a broad hump centered at 130 K. All of these results suggest that there exists an optimal doping with maximum \( T_c \). \( T_c \) increases with increasing pressure for the underdoped sample, and monotonically decreases in the overdoped range. The resistivity hump shifts to high temperature with increasing pressure.

Single crystal \( A_xFe_2Se_2 \) (\( A = K, Cs \)) was grown by the self-flux method, as described elsewhere [17]. Many shining plate-like single crystals can be cleaved from the final products. \( Cs_xFe_2Se_2 \) shows superconductivity at about 30 K, and the actual composition determined by EDX is \( Cs_{0.86}Fe_{1.66}Se_2 \). Two different types of \( K_xFe_2Se_2 \) were obtained. The actual composition of the first one with \( T_c^{onset} = 32.6 \) K is \( K_{0.85}Fe_2Se_{1.80} \) (denoted as \( K_xFe_2Se_2-1 \)). The actual composition of the second one with \( T_c^{onset} = 31.1 \) K is \( K_{0.86}Fe_2Se_{1.82} \) (denoted as \( K_xFe_2Se_2-2 \)). Pressure was generated in a Teflon cup filled with Daphne Oil 7373, which was inserted into a Be-Cu pressure cell. The pressure was determined at low temperature by monitoring the shift in superconducting transition temperature of pure tin. The measurement of resistivity was carried out using Quantum Design PPMS-9.

Figures 1(a)–(c) show the temperature dependence of the in-plane resistivity for single crystal \( Cs_xFe_2Se_2 \), \( K_xFe_2Se_2-1 \) and \( K_xFe_2Se_2-2 \) under different pressures. \( K_xFe_2Se_2-1 \) shows semiconducting behavior at high temperature, shows a broad hump at about 245 K under ambient pressure and shows superconductivity at 32.6 K. The resistivity gradually decreases and the hump becomes much more obscure with increasing pressure. For \( K_xFe_2Se_2-2 \), the broad hump occurs at 130 K and \( T_c^{onset} \) is 31.1 K. For \( Cs_xFe_2Se_2 \), similar resistivity behavior was observed with the broad hump centered at around 285 K. With increasing
Figure 1. Temperature dependence of the in-plane resistivity under different pressures for the single crystals (a) Cs$_x$Fe$_2$Se$_2$, (b) K$_x$Fe$_2$Se$_2$-1 and (c) K$_x$Fe$_2$Se$_2$-2.

pressure, resistivity remarkably decreases and the hump feature becomes much more obscure.

Figure 2(a) shows the temperature dependence of the resistivity of Cs$_x$Fe$_2$Se$_2$ under different pressures in the low temperature range. This indicates that the resistivity gradually

New Journal of Physics 13 (2011) 033008 (http://www.njp.org/)
Figure 2. (a) Temperature dependence of resistivity for single crystal Cs$_x$Fe$_2$Se$_2$ under different pressures around the superconducting transition temperature range. (b) Pressure dependence of $T_c$ for single crystal Cs$_x$Fe$_2$Se$_2$.

decreases with increasing pressure. We defined the $T_c$ with the temperature at which the resistivity drops by 90, 50 and 10% relative to the resistivity just above the superconducting transition. Figure 2(b) shows the pressure dependence of $T_c$. $T_c$ increases with increasing pressure below 0.82 GPa and $T_c$ gradually decreases with further increasing the pressure. $T_c^{onset}$ increases to 31.1 K under the pressure of 0.82 GPa from the 30 K at ambient pressure. The $dT_c/dP \sim 1.3$ K GPa$^{-1}$ in the region of $P < 0.82$ GPa is much less than that in FeSe and almost the same as that observed in electron-doped LaOFeAs [27]. The pressure dependence of $T_c$ in Cs$_x$Fe$_2$Se$_2$ is quite similar to that of the LaO$_{1-x}$F$_x$FeAs system [28].

The temperature dependence of resistivity of K$_x$Fe$_2$Se$_2$-1 under different pressures in the low temperature range is shown in figure 3(a). The resistivity gradually decreased with increasing pressure in the normal state. Figure 3(b) shows the pressure dependence of $T_c$. $T_c$ monotonically decreases with increasing pressure, being different from that shown in
Figure 3. (a) Temperature dependence of resistivity for single crystal $K_xFe_2Se_2-1$ under different pressures around the superconducting transition temperature range. (b) Pressure dependence of $T_c$ for single crystal $K_xFe_2Se_2-1$.

Figure 2(b) for $Cs_xFe_2Se_2$. $T_{c\text{onset}}$ decreases to 29.8 K at the pressure of 1.64 GPa, which is about 2.8 K lower than the $T_{c\text{onset}}$ at ambient pressure. The behavior of $T_c$ versus pressure for this compound is consistent with the results of Guo et al [26], whereas it is quite different from the results of Kawasaki et al [29]. Kawasaki et al reported that $T_{c\text{onset}}$ increases with increasing pressure, while $T_{c\text{zero}}$ decreases. This suggests that the superconducting transition broadens with increasing pressure. However, the superconducting transition width of $K_xFe_2Se_2-1$ remains nearly unchanged with variation of pressure, as shown in figure 3(a). Such a difference could arise from the quality of the single crystal or the inhomogeneity of applied pressure [30, 31].

Figure 4(a) shows the temperature dependence of resistivity of $K_xFe_2Se_2-2$ under different pressures around the temperature range of superconducting transition. The $T_c$ at ambient pressure is 1.5 K less than that of $K_xFe_2Se_2-1$. The behavior of $T_c$ versus pressure is quite different from that of $K_xFe_2Se_2-1$, as shown in figure 3(b). $T_c$ as a function of pressure shows
Figure 4. (a) Temperature dependence of resistivity for single crystal K$_x$Fe$_2$Se$_2$-2 under different pressures around the superconducting transition temperature range. (b) Pressure dependence of $T_c$ for single crystal K$_x$Fe$_2$Se$_2$-2.

Figure 5 shows the pressure dependence of the resistivity hump temperature for Cs$_x$Fe$_2$Se$_2$, K$_x$Fe$_2$Se$_2$-1 and K$_x$Fe$_2$Se$_2$-2. We defined the hump temperature when the resistivity reached its onset gradually increases with increasing pressure and reaches the maximum value of 32.7 K at the pressure of 0.48 GPa and then monotonically decreases with further increasing pressure. It should be noted that the K$_x$Fe$_2$Se$_2$-1 and K$_x$Fe$_2$Se$_2$-2 show different pressure dependences of $T_c$. Such a different pressure dependence of $T_c$ indicates that there occurs optimal doping with the maximum $T_c \sim 32.7$ K in the K$_x$Fe$_2$Se$_2$ system. The pressure tends to destroy the magnetic transition in the undoped compounds and $T_c$ increases with increasing pressure for underdoped iron-pnictides and monotonically decreases in the overdoped region. The different effects of pressure on $T_c$ between the crystals K$_x$Fe$_2$Se$_2$-1 and K$_x$Fe$_2$Se$_2$-2 is easily understood because K$_x$Fe$_2$Se$_2$-1 is in the slightly overdoped range, while K$_x$Fe$_2$Se$_2$-2 is in the underdoped range.
Figure 5. Pressure dependence of the resistivity hump temperature for single crystals Cs$_x$Fe$_2$Se$_2$, K$_x$Fe$_2$Se$_2$-1 and K$_x$Fe$_2$Se$_2$-2.

maximum value. The temperature of the hump monotonically increases with increasing pressure for all the samples. The shift of the resistivity hump temperature for Cs$_x$Fe$_2$Se$_2$ is very small below 0.82 GPa and increases apparently in the high pressure range. The temperature of the hump shows no direct connection with $T_c$ because the pressure dependence of hump temperature is quite different from that of $T_c$. The hump in this kind of superconductor could arise from the content of K or the vacancy of Fe or Se sites.

The normal state resistivity behavior and pressure dependence of $T_c$ are quite different for the crystals K$_x$Fe$_2$Se$_2$ with different $T_c$. The $T_c$ as a function of pressure for K$_x$Fe$_2$Se$_2$-2 shows a dome-like behavior and reaches its maximum $T_c$ at the pressure of 0.48 GPa. In contrast, $T_c$ is gradually suppressed with increasing pressure for K$_x$Fe$_2$Se$_2$-1. The pressure dependence of $T_c$ for K$_x$Fe$_2$Se$_2$-2 and Cs$_x$Fe$_2$Se$_2$ is quite similar to that observed in the LaO$_{1-x}$F$_x$FeAs and parent iron-pnictides [24, 28, 32]. In contrast, for K$_x$Fe$_2$Se$_2$-1, the pressure dependence of $T_c$ is similar to that observed in the overdoped iron-pnictides [33]. The maximum $T_c$ for the two batches of single crystals K$_x$Fe$_2$Se$_2$ is the same, and is reached at ambient pressure and 0.48 GPa, respectively. The difference in $T_c$ between the two batches of single crystal K$_x$Fe$_2$Se$_2$ is very small (just 1.5 K), while the temperature of the resistivity hump is 245 and 130 K, respectively. This indicates that the hump temperature strongly depends on the sample. The hump behavior could originate from the vacancy of Fe or Se. Another piece of evidence is that the normal state resistivity is very high compared with other iron-pnictide superconductors because the vacancy in conducting FeSe layers leads to a strong scattering and consequently high resistivity. This suggests that the physical behavior of A$_x$Fe$_2$Se$_2$ is very sensitive to the deficiency, and a change in the deficiency strongly affects the normal state resistivity although the $T_c$ does not change too much.

In conclusion, we carried out the high-hydrostatic-pressure resistivity measurement for the newly discovered superconductors A$_x$Fe$_2$Se$_2$ (A = K, Cs). For Cs$_x$Fe$_2$Se$_2$, $T_c$ starts to increase at a pressure less than 0.82 GPa, and decreases with further increasing the pressure. This behavior is similar to that in K$_x$Fe$_2$Se$_2$-2. In contrast, the behavior is quite different for K$_x$Fe$_2$Se$_2$-1 with $T_{c\text{ onset}} = 32.6$ K, for which $T_c$ monotonically decreases with increasing pressure. The difference
in pressure dependence of $T_c$ between these single crystals is because they are at different doping levels with different $T_c$. The temperature of the resistivity hump increases with increasing pressure. The resistivity hump could arise from the deficiency in Fe or Se in the conducting layers.

**Acknowledgments**

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

**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** 761
[3] Ren Z A et al 2008 Chin. Phys. Lett. **25** 2215
[4] Liu R H et al 2008 Phys. Rev. Lett. **101** 087001
[5] Rotter M, Tegel M and Johrendt D 2008 Phys. Rev. Lett. **101** 107006
[6] 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
[7] Tapp J H, Tang Z, Lv B, Sasmal K, Lorenz B, Paul Chu C W and Guloy A M 2008 Phys. Rev. B **78** 060505
[8] Parker D R, Pitcher M J, Baker P J, Franke I, Lancaster T, Blundell S J and Clarke S J 2009 Chem. Commun. **2189–91**
[9] Hsu F C et al 2008 Proc. Natl Acad. Sci. **105** 14262
[10] Medvedev S et al 2009 Nat. Mater. **8** 630
[11] Masaki S, Kotehawa H, Hara Y, Tou H, Murata K, Mizuguchi Y and Takano Y 2009 J. Phys. Soc. Japan **78** 063704
[12] Braithwaite D, Salce B, Lapertot G, Bourdarot F, Marin C, Aoki D and Hanfland M 2009 J. Phys.: Condens. Matter **21** 232202
[13] Garbarino G, Sow A, Lejay P, Sulpice A, Toulemonde P, Mezouar M and Nunez-Regueiro M 2009 Eur. Phys. Lett. **86** 27001
[14] Guo J, Jin S, Wang G, Wang S, Zhu K, Zhou T, He M and Chen X 2010 Phys. Rev. B **82** 180520
[15] Mizuguchi Y, Takeya H, Kawasaki Y, Ozaki T, Tsuda T, Yamaguchi T and Takano Y 2011 Appl. Phys. Lett. **98** 042511
[16] Wang A F et al 2010 arXiv:1012.5525 (unpublished)
[17] Ying J J et al 2010 arXiv:1012.5552 (unpublished)
[18] Krzton-Maziopa A, Shermadini Z, Pomjakushina E, Pomjakushin V, Bendele M, Amato A, Khasanov R, Luetkens H and Conder K 2011 J. Phys.: Condens. Matter **23** 052203
[19] Fang M, Wang H, Dong C, Li Z, Feng C, Chen J and Yuan H Q 2010 arXiv:1012.5236
[20] Chu C W and Lorenz B 2009 Physica C **469** 385–C395
[21] Takabayashi Y, McDonald M T, Papanikolaou D, Margadonna S, Wu G, Liu R H, Chen X H and Prassides K 2008 J. Am. Chem. Soc. **130** 9242
[22] Park T, Park E, Lee H, Klimczuk T, Bauer E D, Ronning F and Thompson J D 2008 J. Phys.: Condens. Matter **20** 322204
[23] Alireza P L, Chris Ko Y T, Gillett J, Petrone C M, Cole J M, Lonzarich G G and Sebastian S E 2009 J. Phys.: Condens. Matter **21** 012208
[24] Kurita N, Kimata M, Kodama K, Harada A, Tomita M, Suzuki H S, Matsumoto T, Murata K, Uji S and Terashima T 2010 arXiv:1008.0684
[25] Imai T, Ahilan K, Ning F L, McQueen T M and Cava R J 2009 Phys. Rev. Lett. **102** 177005

*New Journal of Physics* **13** (2011) 033008 (http://www.njp.org/)
[26] Guo J, Sun L, Zhang C, Guo J, Chen X, Wu Q, Gu D, Gao P, Dai X and Zhao Z 2011 arXiv:1101.0092
[27] Lu W, Yang J, Dong X L, Ren Z A, Che G C and Zhao Z X 2008 New J. Phys. 10 063026
[28] Takahashi H, Igawa K, Arii K, Kamihara Y, Hirano M and Hosono H 2008 Nature 453 376
[29] Kawasaki Y, Mizuguchi Y, Deguchi K, Watanabe T, Ozaki T, Tsuda S, Yamaguchi T, Takeya H and Takano Y 2011 arXiv:1101.0896
[30] Matsubayashi K, Katayama N, Ohgushi K, Yamada A, Munakata K, Matsumoto T and Uwatoko Y 2009 J. Phys. Soc. Japan 78 073706
[31] Braithwaite D, Salce B, Lapertot G, Bourdarot F, Marin C, Aoki D, Hanfland M, Wolf T and Sugawara H 2010 Physica C 470 S482
[32] Takahashi H, Okada H, Igawa K, Arii K, Kamihara Y, Matsuishi S, Hirano M, Hosono H, Matsubayashi K and Uwatoko Y 2008 J. Phys. Soc. Japan Suppl. C 77 78–83
[33] Gooch M, Lv B, Lorenz B, Guloy A M and Chu C W 2008 Phys. Rev. B 78 180508