Pressure effect on superconductivity of $A_x Fe_2 Se_2$ (A = K and Cs)

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Abstract. We have performed high hydrostatic pressure resistivity measurements (up to 1.7 GPa) on the newly discovered superconductor $A_x Fe_2 Se_2$ (A = K and Cs) single crystals. Two batches of single crystals $K_x Fe_2 Se_2$ 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 $K_x Fe_2 Se_2$ system. The behavior of T_c versus pressure for $Cs_x Fe_2 Se_2$ 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.

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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 AeFe$_2$As$_2$ (Ae 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 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$_2$As$_2$ (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$_2$Se$_2$. 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$_x$Fe$_2$Se$_2$ and Cs$_x$Fe$_2$Se$_2$. It is found that the transition temperature slightly increases below 0.82 GPa and gradually decreases with further increasing the pressure for Cs$_x$Fe$_2$Se$_2$. Two K$_x$Fe$_2$Se$_2$ single crystals with different T_c were measured. For the K$_x$Fe$_2$Se$_2$ 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$_x$Fe$_2$Se$_2$, T_c^{onset} reaches its maximum value of 32.7 K under the pressure of 0.48 GPa for the K$_x$Fe$_2$Se$_2$ 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$_2$Se$_2$ (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$_x$Fe$_2$Se$_2$ 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$_x$Fe$_2$Se$_2$ were obtained. The actual composition of the first one with $T_c^{onset} = 32.6$ K is K$_{0.85}$Fe$_2$Se$_{1.80}$ (denoted as K$_x$Fe$_2$Se$_2$-1). The actual composition of the second one with $T_c^{onset} = 31.1$ K is K$_{0.86}$Fe$_2$Se$_{1.82}$ (denoted as K$_x$Fe$_2$Se$_2$-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$_x$Fe$_2$Se$_2$, K$_x$Fe$_2$Se$_2$-1 and K$_x$Fe$_2$Se$_2$-2 under different pressures. K$_x$Fe$_2$Se$_2$-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$_x$Fe$_2$Se$_2$-2, the broad hump occurs at 130 K and T_c^{onset} is 31.1 K. For Cs$_x$Fe$_2$Se$_2$, similar resistivity behavior was observed with the broad hump centered at around 285 K. With increasing
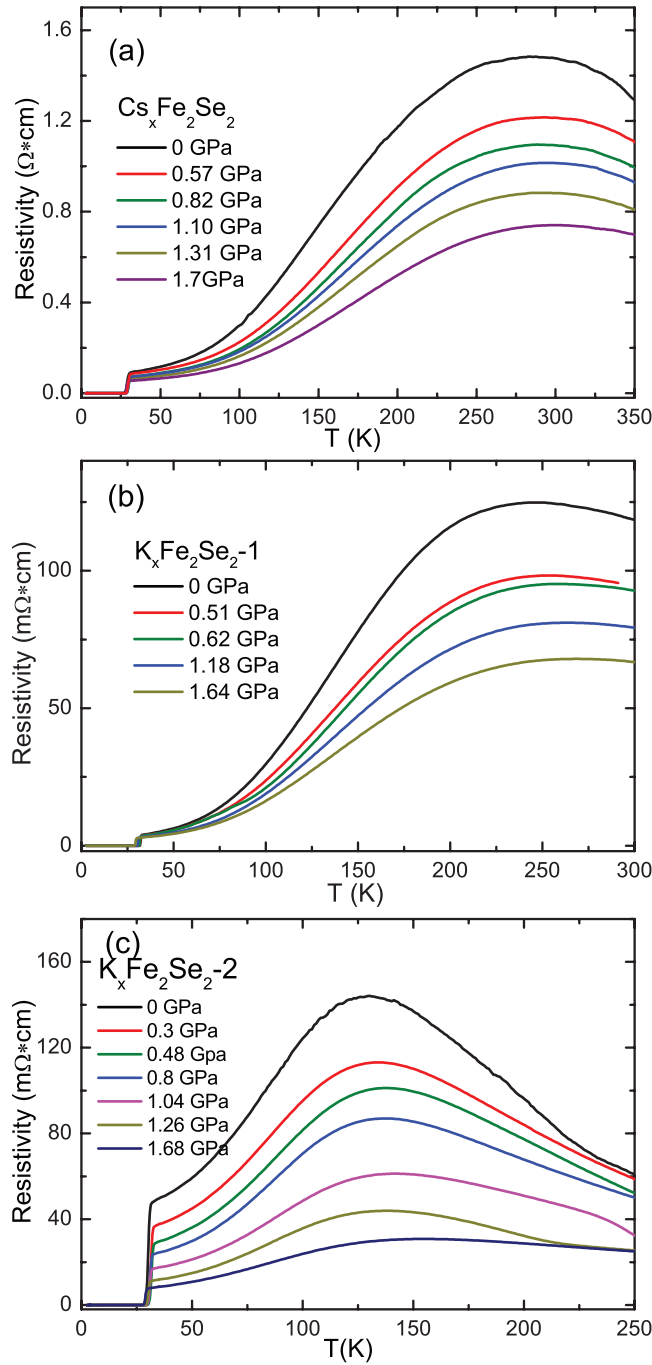
Figure 1. Temperature dependence of the in-plane resistivity under different pressures for the single crystals (a) $Cs_xFe_2Se_2$, (b) $K_xFe_2Se_2$-1 and (c) $K_xFe_2Se_2$-2.

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

Figure 2(a) shows the temperature dependence of the resistivity of $Cs_xFe_2Se_2$ under different pressures in the low temperature range. This indicates that the resistivity gradually

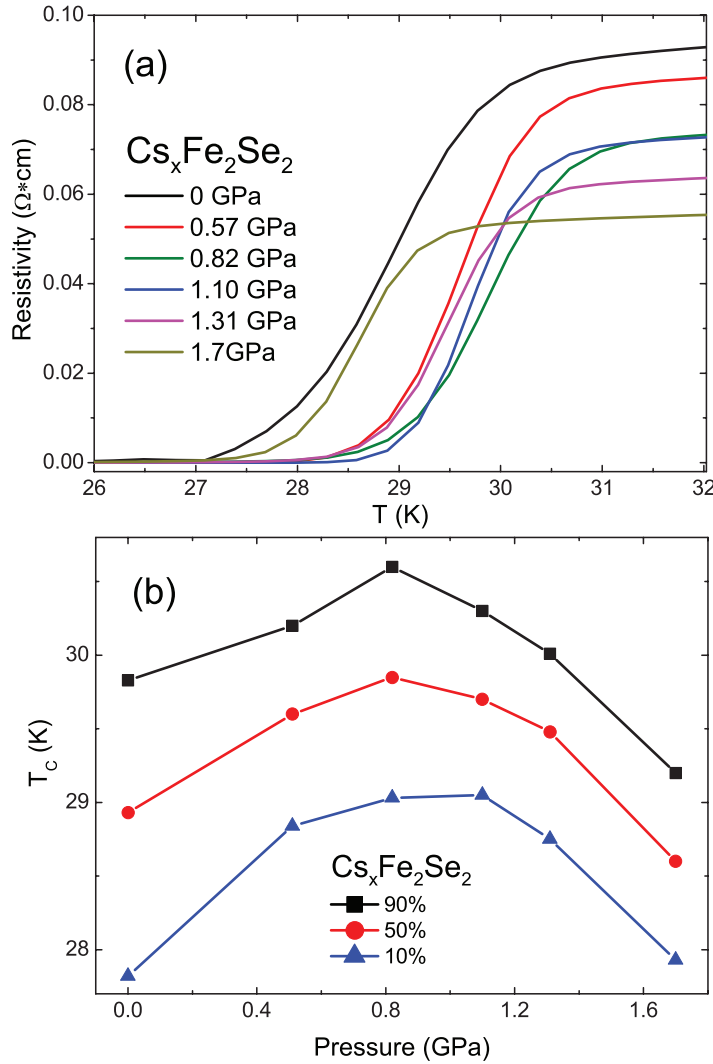**Figure 2.** (a) Temperature dependence of resistivity for single crystal $Cs_xFe_2Se_2$ under different pressures around the superconducting transition temperature range. (b) Pressure dependence of T_c for single crystal $Cs_xFe_2Se_2$.

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 $Cs_xFe_2Se_2$ is quite similar to that of the $LaO_{1-x}F_xFeAs$ system [28].

The temperature dependence of resistivity of $K_xFe_2Se_2$-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
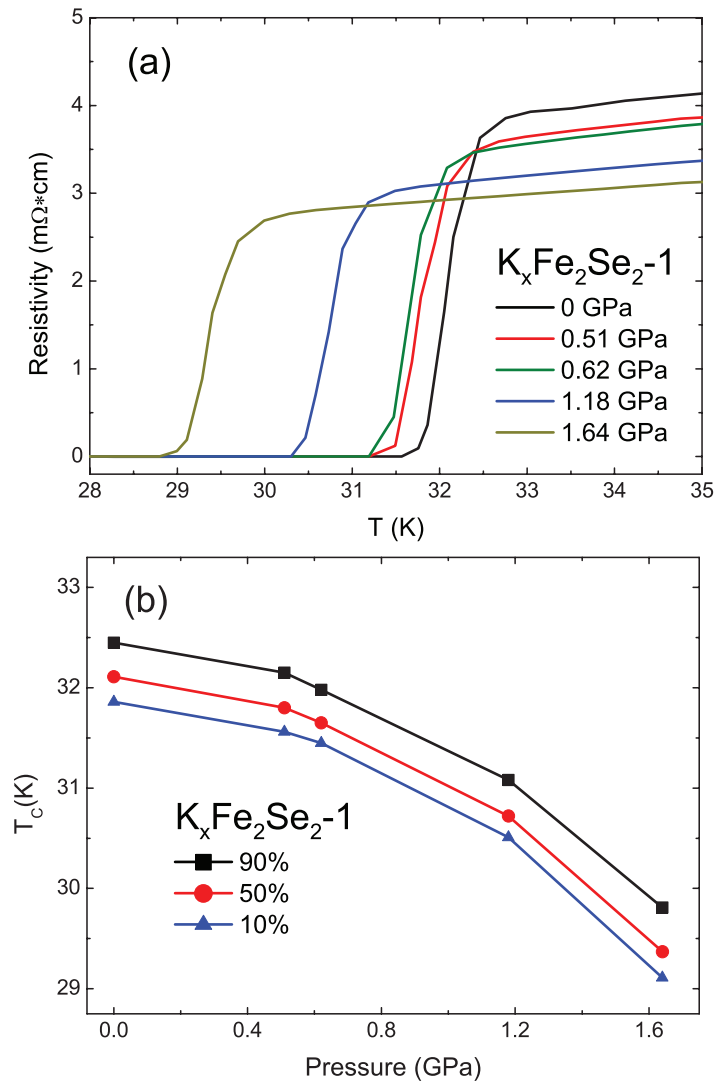
Figure 3. (a) Temperature dependence of resistivity for single crystal $K_x Fe_2 Se_2$-1 under different pressures around the superconducting transition temperature range. (b) Pressure dependence of T_c for single crystal $K_x Fe_2 Se_2$-1.

figure 2(b) for $Cs_x Fe_2 Se_2$. T_c^{onset} decreases to 29.8 K at the pressure of 1.64 GPa, which is about 2.8 K lower than the T_c^{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^{onset} increases with increasing pressure, while T_c^{zero} decreases. This suggests that the superconducting transition broadens with increasing pressure. However, the superconducting transition width of $K_x Fe_2 Se_2$-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 $K_x Fe_2 Se_2$-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 $K_x Fe_2 Se_2$-1. The behavior of T_c versus pressure is quite different from that of $K_x Fe_2 Se_2$-1, as shown in figure 3(b). T_c as a function of pressure shows
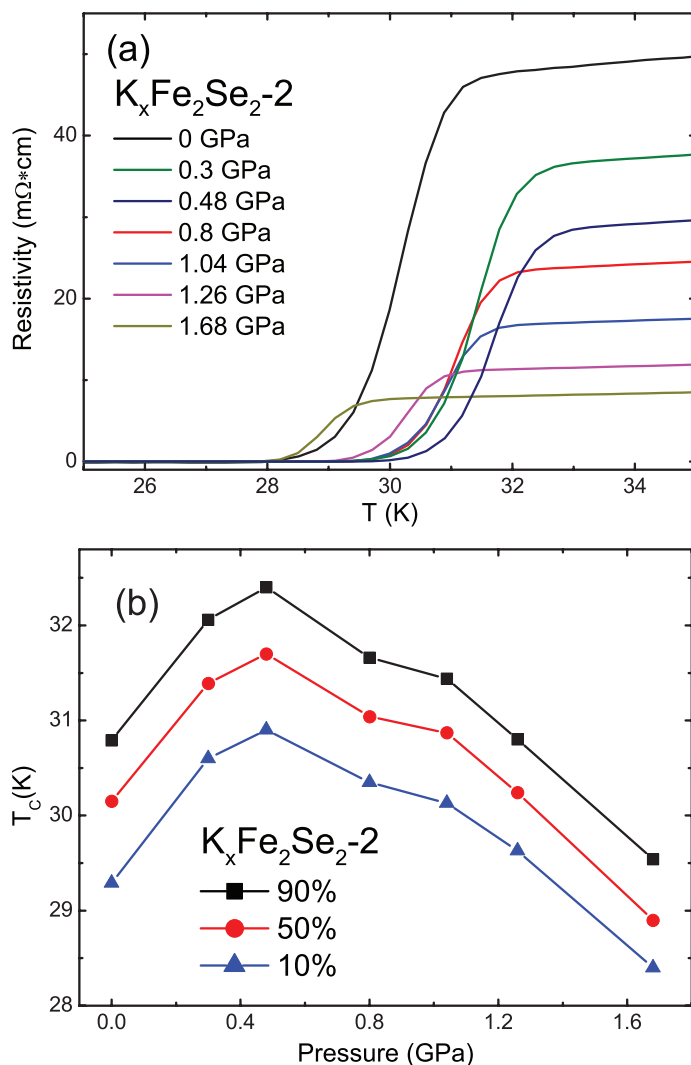
Figure 4. (a) Temperature dependence of resistivity for single crystal $K_x Fe_2 Se_2$-2 under different pressures around the superconducting transition temperature range. (b) Pressure dependence of T_c for single crystal $K_x Fe_2 Se_2$-2.

a dome-like behavior, as shown in figure 4(b). It is similar to that observed in single crystal $Cs_x Fe_2 Se_2$. T_c^{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 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
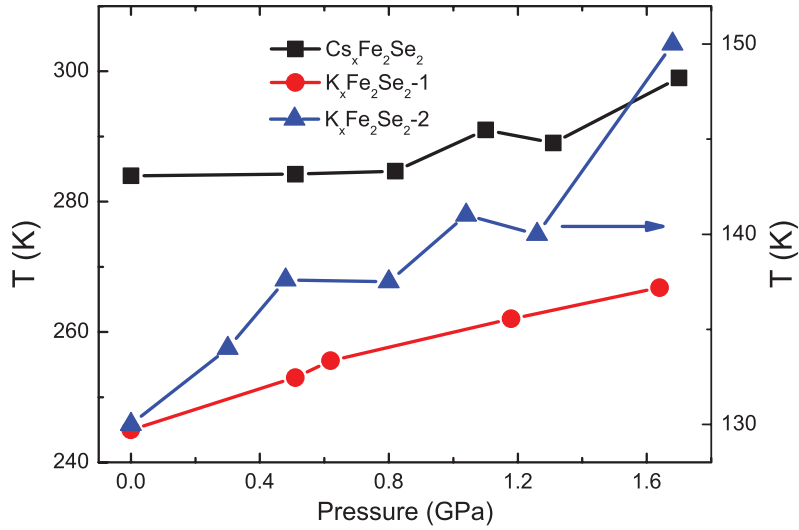
Figure 5. Pressure dependence of the resistivity hump temperature for single crystals $Cs_xFe_2Se_2$, $K_xFe_2Se_2$-1 and $K_xFe_2Se_2$-2.

maximum value. The temperature of the hump monotonically increases with increasing pressure for all the samples. The shift of the resistivity hump temperature for $Cs_xFe_2Se_2$ 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 $K_xFe_2Se_2$ with different T_c. The T_c as a function of pressure for $K_xFe_2Se_2$-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 $K_xFe_2Se_2$-1. The pressure dependence of T_c for $K_xFe_2Se_2$-2 and $Cs_xFe_2Se_2$ is quite similar to that observed in the $LaO_{1-x}F_xFeAs$ and parent iron-pnictides [24, 28, 32]. In contrast, for $K_xFe_2Se_2$-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 $K_xFe_2Se_2$ 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 $K_xFe_2Se_2$ 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 $A_xFe_2Se_2$ 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 $A_xFe_2Se_2$ (A = K, Cs). For $Cs_xFe_2Se_2$, 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 $K_xFe_2Se_2$-2. In contrast, the behavior is quite different for $K_xFe_2Se_2$-1 with $T_c^{onset} = 32.6$ 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

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