Transport properties of FeSe$_{1-x}$S$_x$ and FeSe$_{1-y}$Te$_y$ epitaxial thin films under magnetic fields

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Abstract. We comparatively investigated transport properties of FeSe$_{1-x}$S$_x$ and FeSe$_{1-y}$Te$_y$ epitaxial thin films under magnetic field. The contrastive behavior between Te and S substituted materials was observed in the carrier density estimated from the Hall effect as a function of $x$ (or $y$), which is similar to that in $T_c$. This means that the effect of the disappearance of the structural transition is not universal for superconductivity in Fe chalcogenides. $T_c$ was found to have a strong correlation with carrier concentration, which is in agreement with our recent result in FeSe film samples where the strain was changed systematically from compressive to tensile.

1. Introduction
Since the discovery of superconductivity in LaFeAs(O,F), iron based superconductors (FeSCs) have attracted much attention[1]. FeSe is a suitable material for understanding the origin of the superconductivity in FeSCs because it has the simplest crystal structure among FeSCs. The superconducting transition temperature, $T_c$, is about 9 K at ambient pressure[2]. Unlike other FeSCs, FeSe exhibits the tetragonal-orthorhombic structural phase transition (SPT) at about 90 K without antiferromagnetic (AFM) order. The SPT is considered to have an electronic origin and is often called as the nematic transition[3]. FeSe$_{1-y}$Te$_y$ has been investigated intensively from the early stage[4], and Te substitution increased $T_c$ up to $\sim$ 14K. However there is a miscibility gap at $0.1 \leq y \leq 0.4$ in bulk crystals[4], and the relation between the superconductivity and the SPT was unclear. We have successfully fabricated FeSe$_{1-y}$Te$_y$ thin films for all $y$ values[5]. Interestingly, $T_c$ rapidly increased with increasing Te content at the composition where the SPT disappears[6]. This may suggest that the SPT suppress the superconductivity. On the other hand, FeSe$_{1-x}$S$_x$ bulk samples do not show such a sudden increase of $T_c$ at the SPT[7]. We recently found that FeSe$_{1-x}$S$_x$ films also show a gradual decrease of $T_c$ with increasing $x$ even at the SPT[8]. These results indicate that the relation between the superconductivity and the SPT is not universal in iron chalcogenides. To clarify the relation between the superconductivity and the SPT, we investigate the magneto-transport phenomena (Hall effect and magnetoresistance) in these samples. It is found that the carrier densities, $n$ and $p$, increase as Te content increases, while they remain almost unchanged for S substituted samples. These mean that $T_c$ has a strong correlation with carrier concentration, which is in agreement with our recent result in FeSe films where the strain was changed systematically from compressive to tensile. Therefore, it is essential to increase the carrier concentration for the $T_c$ enhancement of iron chalcogenides.
2. Method
FeSe$_{1-x}$S$_x$ and FeSe$_{1-y}$Te$_y$ epitaxial films were grown on LAO substrate by the pulse laser deposition (PLD) method with a KrF laser[6, 8, 10]. The back pressure of the growth chamber is approximately $\sim 10^{-8}$ Torr. For FeSe$_{1-x}$S$_x$ growth, Fe$_{1.1}$Se and FeS polycrystalline pellets were used as targets[8]. Single-phase FeSe$_{1-x}$S$_x$ films were obtained by ablatting each target alternatively[9]. On the other hand, stoichiometric FeSe$_{1-y}$Te$_y$ target were used for FeSe$_{1-y}$Te$_y$. The $a$-axis and the $c$-axis lengths of the films were determined from the 204 or the 111 reflection peaks and the 00l reflection peaks in the X-ray diffraction (XRD) measurements. The thickness of the films was 40 $\sim$ 100 nm, which was estimated from X-ray reflectivity (XRR) measurements or by a Dektak 6 M stylus profiler. These films were deposited in a six-terminal shape using a metal mask for transport measurements. The measured area was 1.2 mm long and 1.0 mm wide. The electrical resistivity and the transport properties were measured using a Physical Property Measurement System (PPMS, Quantum Design, Inc.).

3. Result and Discussion
Figure 1 shows the temperature dependence of the resistivity of the grown films. All films show the metallic behavior and the superconducting transition. FeSe$_{1-x}$S$_x$ with $x \leq 0.14$ and FeSe$_{1-y}$Te$_y$ with $y \leq 0.20$ show a kink anomaly which corresponds to the SPT. On the other hand, FeSe$_{1-x}$S$_x$ with $x = 0.19$ and 0.25 and FeSe$_{1-y}$Te$_y$ with $y = 0.30$ and 0.40 do not show the SPT. The $x = 0.25$ S-substituted sample shows another kink anomaly in the $\rho \sim T$ curve at low temperatures. This kink structure is characteristic of film samples, and is considered to originate from the AFM transition[8]. Figures 2(a) and (b) show the temperature dependence of the Hall coefficient $R_H$ of the FeSe$_{1-x}$S$_x$ and FeSe$_{1-y}$Te$_y$ films. The obtained behavior is very contrastive between the Te-substituted system and the S-substituted system, in particular in the tetragonal phase. In both systems, $R_H$ increases rapidly with decreasing temperature in the orthorhombic phase. In the samples without the SPT (all in the tetragonal phase), however, the $R_H$ of the Te substituted samples stay very small and even becomes negative at low temperatures (essentially the same behavior was observed in the Te substituted films grown on CaF$_2$[10]), whereas the $R_H$ of the S-substituted samples increases at low temperatures. This behavior is similar to the one in the orthorhombic phase. These suggest that the effect of the SPT on the electronic structure is rather different between the Te-substituted system and the S-substituted system.

Figure 3 shows the magnetic field-dependence of the magnetoconductance of the typical two representative films (one Te-substituted and the other S-substituted). Both films show the
Figure 2. Temperature dependence of the Hall coefficient $R_H$ of (a) FeSe$_{1-x}$S$_x$ thin films and (b) FeSe$_{1-y}$Te$_y$ thin films grown on LAO substrate.

Figure 3. The magnetoresistance of the FeSe$_{0.86}$S$_{0.14}$ and FeSe$_{0.90}$Te$_{0.10}$ thin films on LAO substrate as a function of the magnetic field at $T$ = 30 K.

quadratic dependence. This suggests that we can assume a simple two-band picture of an electron and a hole. Indeed, it is well established that in iron-chalcogenides, the multiple bands contribute to the electrical transport properties such as the Hall coefficient and the magnetoresistance. As the simplest approach, the two band picture of the electron and the hole is often worked with. Therefore, using a two band model of one hole band and one electron band, we further investigate the nature of the charge carriers.
The resistivity tensor is written as

\[
\rho_{xx}(0) = \frac{1}{e(n_e\mu_e + n_h\mu_h)} \tag{1}
\]

\[
\rho_{xx}(B) = \frac{-n_e\mu_e^2 + n_h\mu_h^2}{e(n_e\mu_e + n_h\mu_h)^2}B \tag{2}
\]

\[
\frac{\rho_{xx}(B) - \rho_{xx}(0)}{\rho_{xx}(0)} = \frac{n_e n_h \mu_e \mu_h (\mu_e + \mu_h)^2}{(n_e\mu_e + n_h\mu_h)^2} B^2 \tag{3}
\]

where \(\mu_h, \mu_e, n_h, n_e\) are the hole mobility, the electron mobility, the hole density and the electron density, respectively. To solve these three equations on four parameters, we need to assume that \(n_h\) is proportional to \(n_e\). For simplicity, we assume \(n_h = n_e\). The different choice for the magnitude of the proportionality constant does not affect the result largely[13].

Magnetoresistance is more remarkable at lower temperatures. However, avoiding the effect of superconductivity, we work with the data at 30 K.

![Figure 4](image-url)

**Figure 4.** (a) \(T_c^{\text{onset}}\) and (b) \(n_e\) and \(n_h\), and (c) \(\mu_e\) and \(\mu_h\) at 30 K as functions of S content \(x\) and Te content \(y\). The dashed lines show the boundary between the orthorhombic and tetragonal phases. The data of the bulk samples of FeSe\(_{1-x}\)S\(_x\) [11, 12] are also plotted. The upper triangle is the data from[11] at 25 K, and the lower triangle is the data from[12]at 15 K.

Figures 4 (a), (b) and (c) show \(T_c^{\text{onset}}\), the carrier densities, \(n_e\) and \(n_h\), and the mobilities, \(\mu_e\) and \(\mu_h\), as a function of S content and Te content, respectively. The contrastive behavior of \(T_c^{\text{onset}}\) at the SPT between S-substituted samples and Te-substituted samples is observed. What is remarkable is that the similar contrastive behavior is observed in the carrier density as a function of substitution amount. In FeSe\(_{1-x}\)S\(_x\), \(n_e\) (and \(n_h\)) does not depend largely, and is rather almost independent of \(x\) both in the orthorhombic and in the tetragonal phase. On the other hand, in FeSe\(_{1-y}\)Te\(_y\), \(n_e\) (and \(n_h\)) increases in the tetragonal phase. These behaviors of \(n_e\) (and \(n_h\)) correspond well with the characteristic dependence of \(T_c\) on \(n_e\) (and \(n_h\)). Such remarkable features were not observed in the mobility. Both of \(\mu_e\) and \(\mu_h\) decrease systematically with increasing substitution amount in both cases of FeSe\(_{1-x}\)S\(_x\) and FeSe\(_{1-y}\)Te\(_y\), and no significant change was observed at the SPT. We previously observed the similar remarkable correlation of \(T_c\) with the carrier density in FeSe films with various degrees of strain introduced systematically[13].

These results suggest the close relation between \(T_c\) and the carrier density in iron chalcogenides. We already mentioned, based on our results, that the electron nematicity does
not play a universally significant role on superconductivity in Fe chalcogenides. The results presented here suggests that the SPT affects on the electronic structure differently between Te substituted and S substituted samples. This is the direct origin of the difference of $T_c$ behavior at the SPT, manifested in the close correlation between $T_c$ and the carrier density.

4. Conclusion
We comparatively investigated transport properties of FeSe$_{1-x}$S$_x$ and FeSe$_{1-y}$Te$_y$ epitaxial thin films under magnetic field. The contrastive behavior between Te and S substituted materials was observed in the carrier density estimated from the Hall effect as a function of x (or y), which is similar to that in $T_c$. This means that the effect of the disappearance of the structural transition is not universal for superconductivity in Fe chalcogenides. $T_c$ was found to have a strong correlation with carrier concentration, which is in agreement with our recent result in FeSe films where the strain was changed systematically from compressive to tensile.

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