Effects of disorder in Fe$_x$Ti(Se$_{1-y}$S$_y$)$_2$ single crystals

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Abstract. We investigate the effects of disorder in Fe$_x$Ti(Se$_{1-y}$S$_y$)$_2$ single crystals. In M$_x$TiSe$_2$ ($M = Fe, Co, and Ni$), positive magnetoresistance proportional to magnetic field and power-law scaling of magnetization were observed. This observation has been attributed to disorder-induced distribution of Kondo temperature, which causes effective Kondo temperature much lower than single-ion Kondo temperature $T_K$ and which also results in non-Fermi liquid properties in M$_x$TiSe$_2$ below the percolation threshold ($x < x_c$). Fe$_x$Ti(Se$_{1-y}$S$_y$)$_2$, which connects magnetic phases in Fe$_x$TiS$_2$ with the disordered Kondo region in Fe$_x$TiSe$_2$ is an interesting system which provide a clue about how disorder-dominated Kondo region evolves into various magnetic phases. We discuss this interesting problem on the basis of our recent transport measurements on Fe$_x$Ti(Se$_{1-y}$S$_y$)$_2$ single crystals.

1. Introduction

Layered compounds TiX$_2$ ($X$: chalcogen), which has been known for a long time are interesting materials with low-dimensional electronic structure, easily intercalated with guest atoms [1,2]. Depending on degree of electron transfer from the chalcogens to Ti 3d orbitals and of the $p$-$d$ hybridization, TiS$_2$, TiSe$_2$, and TiTe$_2$ are two-dimensional semiconductor, semimetal, and metal, respectively. Among them, TiSe$_2$ has attracted much attention due to its peculiar charge density wave (CDW). Since its Fermi surface consists of six ellipsoidal pockets, CDW in this compound cannot be understood within a conventional nest picture. In addition, Cu-intercalated TiSe$_2$ (Cu$_x$TiSe$_2$) exhibits superconductivity at around 4.2 K with similar doping dependence of $T_c$ with high-$T_c$ cuprate superconductors [3]. The origin of superconductivity in this compound is still elusive.

The above-mentioned results suggest that intercalation in TiSe$_2$ can be a possible pathway to realize exotic ground states. In this regard, M$_x$TiSe$_2$ ($M =$ magnetic 3d transition metal) is a good candidate for an exotic ground state, where spin and disorder plays an important role. Consistently with this expectation, the interesting interplay between the Kondo effect and randomness of guest magnetic $M$ atoms in M$_x$TiSe$_2$ ($M = Co, Ni, and Fe$) single crystals was reported [4]. Although the typical low-T upturn of resistivity implies the Kondo effect around the single-ion Kondo temperature

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$T_K$, as in conventional Kondo phenomena, positive magnetoresistance linearly proportional to the magnetic field [5] and the power-law scaling of magnetization [6] suggest the forbidden coexistence between Kondo effect and time reversal symmetry breaking. It is revealed that this puzzling result is due to disorder-induced distribution of the Kondo temperature, which produces an effective Kondo temperature ($\tau_K$) much lower than $T_K$. This allows unscreened local moments above $\tau_K$ and results in non-Fermi liquid properties in $M_x\text{TiSe}_2$ below the percolation threshold ($x < x_c$). On the other hands, in the related compound $M_x\text{TiS}_2$, various magnetic phases have been reported, depending on $x$. Therefore, a question naturally emerges how disorder-dominated Kondo region in $M_x\text{TiSe}_2$ evolves into various magnetic phases in $M_x\text{TiS}_2$ when $y$ is varied in $M_x\text{Ti(Se}_{1-y}\text{S}_y)_2$. In this research, we address this issue on the basis of our recent transport measurements.

2. Experiments

The single crystals of Fe$_x\text{Ti(Se}_{1-y}\text{S}_y)_2$ were grown by a chemical vapor transport technique in the presence of iodine as a transport agent. To avoid co-intercalation of guest $M$ atoms and constituent Ti atoms into the host TiSe$_2$, all compounds were grown at relatively low temperature (500 °C). Above that temperature, Ti atoms are known to self-intercalate into the host. Values of the intercalated guest concentration $x$ were determined by electron-probe microanalysis. X-ray powder diffraction measurements for $M_x\text{TiSe}_2$ indicated that these compounds have a 1T-CdI$_2$ structure. Resistivity measurements were performed in the temperature range from 4.2 to 300 K using a DC four-probe method.

![Resistivity curves](image.png)

**Fig. 1** Resistivity curves of (a) Ti(S$_{1-y}$Se$_y$)$_2$ and (b) Fe$_x\text{TiSe}_2$

3. Results and Discussion

Figure 1 shows resistivity curves of (a) Ti(S$_{1-y}$Se$_y$)$_2$ and (b) Fe$_x\text{TiSe}_2$. In TiSe$_2$, a large CDW peak is clearly seen. For S substitution, the CDW peak is gradually suppressed and it moves to lower temperature a little. Even for $y=1/3$, a small hump at around 100 K can be discerned. This indicates that the S substitution is not so effective in killing CDW. The resistivity value at $T = 4.2$ K increases with $y$. However, up to $y = 1/3$, Ti(S$_{1-y}$Se$_y$)$_2$ still shows metallic resistivity curves. It is of importance to understand what influence S substitution makes on CDW.

The effect of Fe intercalation is quite different from that of S substitution. Compared to S substitution, the CDW peak is rapidly suppressed by Fe intercalation and the peak maximum moves to lower temperatures at a fast rate. This implies that Fe intercalation is effective compared with S in killing the CDW. As Fe is intercalated, Fe$_x\text{TiSe}_2$ becomes eventually insulating. For instance, at $x =$
0.065, only the low-T upturn survives while the CDW is completely suppressed. In the previous investigation, this upturn combined with magnetoresistance and magnetization was a signature of disordered Kondo phenomena [4].

In order to investigate effects of S substitution on Fe\textsubscript{\textit{x}}TiSe\textsubscript{2}, we have measured the resistivity of Fe\textsubscript{\textit{x}}Ti(S\textsubscript{0.1}Se\textsubscript{0.9})\textsubscript{2}, Fe\textsubscript{\textit{x}}Ti(S\textsubscript{0.2}Se\textsubscript{0.8})\textsubscript{2}, and Fe\textsubscript{\textit{x}}Ti(S\textsubscript{1/3}Se\textsubscript{2/3})\textsubscript{2} as shown in Fig. 2. As in Ti(S\textsubscript{y}Se\textsubscript{1-y})\textsubscript{2}, the Fe atoms intercalated into Ti(S\textsubscript{y}Se\textsubscript{1-y})\textsubscript{2} suppresses the remaining CDW quickly and further Fe doping induces a metallic state. Interestingly, before approaching a complete metallic state, there exists a charge localized state, where a low-T upturn of the resistivity appears. For example, see the data of \textit{x} \sim 0.05 in Fig. 2. Even though it is rather hard to conclude the nature of this charge localized state with the resistivity data alone, Kondo effect is expected to be crucial as in Fe\textsubscript{\textit{x}}TiSe\textsubscript{2}.

Another notable aspect of this data is that the resistivity for \textit{x} > 0.05 exhibits a metallic resistivity with a linear slope at high temperature and it crosses into the \textit{T}^\alpha dependence at low temperature. Interestingly, the crossover temperature is lowest in case of Fe\textsubscript{\textit{x}}Ti(S\textsubscript{1/3}Se\textsubscript{2/3})\textsubscript{2} among the three compositions. Thus, Fe\textsubscript{\textit{x}}Ti(S\textsubscript{1/3}Se\textsubscript{2/3})\textsubscript{2} shows robust linear temperature-dependence of the resistivity. Although it is too early to conclude the origin of this temperature dependence definitely, the fact that the crossover temperature seems to vary systematically among the three compositions still leaves a possibility for the electronic origin about this. Therefore, it is quite necessary to investigate this problem systematically with more samples with compositions between \textit{x} = 0 and \textit{x} = 0.1. Since Kondo singlet is stabilized on the Se-rich compositions of Fe\textsubscript{\textit{x}}Ti(Se\textsubscript{1-y}S\textsubscript{y})\textsubscript{2} [4] while magnetic phases exist on the S-rich compositions [7], it is expected to observe a phase transition or a crossover in between, which may be correlated with transport properties discussed above.

![Resistivity Curves](image)

**Fig. 2** The resistivity curves of Fe\textsubscript{\textit{x}}Ti(S\textsubscript{0.1}Se\textsubscript{0.9})\textsubscript{2}, Fe\textsubscript{\textit{x}}Ti(S\textsubscript{0.2}Se\textsubscript{0.8})\textsubscript{2}, and Fe\textsubscript{\textit{x}}Ti(S\textsubscript{1/3}Se\textsubscript{2/3})\textsubscript{2}

**4. Conclusions**
We have reported effects of disorder in Fe$_x$Ti(Se$_{1-y}$S$_y$)$_2$ single crystals. We found that the S substitution is not so effective in suppressing CDW, while Fe intercalation rapidly kills CDW. As in Fe$_x$TiSe$_2$, a charge localized state have been identified from the resistivity data at around $x = 0.05$. Even though it is difficult to conclude the nature of this state definitely now, it is believed that Kondo singlet formation plays an important role as in Fe$_x$TiSe$_2$. When $x$ is varied at a given $y$, an interesting change from a charge localized state to metallic one was observed. It will be important to understand the nature of this crossover point. We suggest to compare results on Fe$_x$Ti(Se$_{1-y}$S$_y$)$_2$ with phenomenology of quantum critical point.

5. References

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