Transport properties in Cu$_x$TiSe$_2$ (0.015≤x≤0.110) Single Crystal

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Transport properties are systematically studied for the single crystals Cu$_x$TiSe$_2$ (0.015≤x≤0.110). Both of in-plane and out-of-plane resistivity show the coexistence of superconducting transition and charge density wave (CDW) for the single crystals with x≤0.025. After CDW state is completely suppressed around x=0.055, the superconductivity is apparently enhanced by Cu doping. No superconducting transition is observed above 1.8 K for Cu$_{0.11}$TiSe$_2$. Anisotropy in resistivity increases with increasing Cu content, and is nearly T-independent. CDW state has a strong effect on Hall coefficient and thermopower. A large thermopower, comparable to the triangle lattice Na$_x$CoO$_2$, is observed in Cu$_x$TiSe$_2$. Intercalation of Cu induces a negative MR due to the interaction between conducting carriers and localized magnetic moments.

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INTRODUCTION

Layered transition metal dichalcogenides (TMD’s) MX$_2$ (M= transition metal, X=S, Se, or Te) have been extensively studied due to its two dimensionality structure and physical properties, such as superconductivity and charge density wave (CDW) transition. The structure of these compounds usually manifests two types of 1T and 2H phase, both of structures are formed by X-M-X sandwiches. The top and bottom sheets are chalcogen atoms, and the middle sheet is metal atom. In 1T phase, all the sandwiches stack to each other as octahedral. While in 2H phase, the sandwiches stack as trigonal prismatic. CDW state is one of the most interesting phenomena observed in TMD’s and widely studied. Superconductivity also appears in some materials, such as 2H-NbS$_2$ which is a multi-gap s-wave superconductor. Coexistence of superconductivity and CDW state has been widely observed in 2H transition metal dichalcogenides: TaSe$_2$, TaS$_2$ and NbS$_2$. 2H-TaSe$_2$ experiences an incommensurate and a commensurate CDW transitions at 122 K and 90 K, respectively; 2H-TaS$_2$ and 2H-NbSe$_2$ undergo only one incommensurate CDW transition at 75 K and 35 K; while 2H-NbS$_2$ shows no CDW transition. In contrast to the CDW transition, the superconducting transition temperature decreases from 2H-TaSe$_2$, through 2H-TaS$_2$ and 2H-NbSe$_2$ to 2H-NbS$_2$, indicating that CDW state and superconductivity compete to each other.

The interaction between the layers of TMD’s is weak van der Waals type, so that this kind of compounds can be easily intercalated by various guest species (eg. alkali metal atom, 3d transition metal atom, or molecules). Lattice parameters are usually changed by intercalation, superstructure can be observed at some guest concentration. Such superstructure is related to the CDW state. Recently, it is found that intercalation of Na into 2H-TaS$_2$ increases the superconducting transition temperature to 5K, and suppresses the CDW transition. Effect of pressure on superconductivity and CDW state shows similar result in 2H-NbSe$_2$. These results further indicate that the superconductivity and CDW state compete to each other.

The intercalation of various guests into van der Waals gaps of MX$_2$ is another way to study TMD’s and to find new phenomenon. Recently, Cu is successfully intercalated into 1T-TiSe$_2$. Intercalation of Cu continuously suppresses the CDW transition, superconductivity emerges in the sample Cu$_x$TiSe$_2$ with x~0.04, and reaches a maximum transition temperature (T$_c$) of 4.15 K at x~0.08, then T$_c$ decreases with further doping Cu. Phase diagram of Cu$_x$TiSe$_2$ is quite similar to that of high T$_c$ cuprates. Therefore, it is of great interest to reveal if unconventional superconductivity exists in Cu$_x$TiSe$_2$ system. Cu$_x$TiSe$_2$ is the first superconducting 1T structured MX$_2$ compound. TiSe$_2$ intercalated with other 3d transition metal (eg: V, Cr, Mn, Fe, Co, Ni) has been reported, but no superconductivity is observed. Study on anisotropic properties of Cu$_{0.07}$TiSe$_2$ shows that it was a normal type II superconductor. The results of thermal conductivity for Cu$_{0.06}$TiSe$_2$ indicate that it is a single-gap s-wave superconductor. ARPES results show that intercalation of Cu could enhance the density of states, leading to the superconductivity, but excessive Cu makes superconductivity disappear due to strong inelastic scattering. In order to understand the CDW state and superconductivity in this novel compound Cu$_x$TiSe$_2$, we made detailed study on transport properties on high quality single crystals Cu$_x$TiSe$_2$. It is found the coexistence of superconducting transition and charge density wave (CDW) for the single crystals with x=0.015 and x=0.025, different from polycrystalline case in which su-

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perconductivity emerges at $x=0.04$.\textsuperscript{[14]} The CDW state shows an apparent effect on resistivity, Hall coefficient and thermopower.

**EXPERIMENT DETAILS**

High quality $\text{Cu}_x\text{TiSe}_2$ single crystals were grown by the chemical iodine-vapor transport method. Powders of Cu (99.7%), Ti (99.5%) and Se (99.5%) were mixed and thoroughly ground, then pressed into pellet. The pellet was sealed under vacuum in a quartz tube with diameter of 13mm and length of 150mm with iodine ($10\text{mg/cm}^3$). One end of tube was slowly heated to 940°C with heating rate of $\sim150^\circ\text{C/h}$, another end of the tube was kept at 740°C. After one week, the furnace was cooled to room temperature over a few hours. Finally many golden plate-like $\text{Cu}_x\text{TiSe}_2$ crystals were obtained. The typical dimensional is about $5\times5\times0.3\text{mm}^3$. Because the element Cu can react with Se very easily, excessive Cu was used as starting material. For example, in order to grow the $\text{Cu}$ $0.055\text{TiSe}_2$ crystals, the stoichiometry of Cu, Ti and Se powder is 0.4:1:2 in molar ratio. Actual composition of the single crystals was determined by X-ray Fluorescence Spectroscopy (XRF) (XRF-1800, Shimadzu Inc.)

All crystals were characterized by Rigaku D/max-A X-Ray diffractometer (XRD) with graphite monochromatized Cu Kα radiation ($\lambda=1.5406\text{Å}$) in the $2\theta$ range of 10−70° with the step of 0.02° at room temperature. Resistivity measurements were performed on a DC resistance bridge (Linear Research, Inc., Model LR700) by the standard four-probe method. The magnetic field was supplied by a superconducting magnet system (Oxford Instruments). Hall contact configuration is the standard ac six-probe geometry. To eliminate the offset voltage due to the asymmetric Hall terminals, the magnetic field was scanned from -5 to 5 T. Thermopower measurements were carried out with a home-built apparatus and performed using small and reversible temperature differences of 0.5K. Two ends of the single crystals were attached to two separated copper heat sinks to generate the temperature gradient along the crystal ab plane. Two Rh-Fe thermometers were glued to the heat sink (next to the single crystals). Copper leads were adhered to the single crystals and all the data were corrected for the contribution of the Cu leads.

**RESULTS AND DISCUSSION**

Figure 1 shows c-axis lattice parameter as a function of Cu content ($x$). The c-axis lattice parameter was obtained by the X-ray diffraction on single crystals $\text{Cu}_x\text{TiSe}_2$ with different $x$. It shows a good relationship between the c-axis lattice parameter and Cu content. The c-axis lattice parameter increases linearly with increasing Cu content. This is consistent with that reported in polycrystalline samples.\textsuperscript{[14]}

![Figure 1](image1.png)

**FIG. 1:** C-axis lattice parameter as a function of $x$ in $\text{Cu}_x\text{TiSe}_2$ for single crystals, being consistent with that reported in polycrystalline samples.\textsuperscript{[14]} The straight line guides eyes.

Figure 2 shows temperature dependence of in-plane resistivity $\rho_{ab}$ from 300 K to 1.8 K for $\text{Cu}_x\text{TiSe}_2$ crystal with different Cu contents ($x=0.015$, 0.025, 0.055, 0.065, 0.08, 0.10 and 0.11). As show in Fig.2(a), $\rho_{ab}$ shows a CDW hump for the samples with $x \leq 0.025$, the CDW hump becomes broader and moves to lower temperature with increasing $x$. For the sample with $x=0.055$, the CDW hump disappears and the resistivity shows nearly $T^2$-dependent. It suggests that CDW state is completely suppressed around $x=0.055$. Intercalation of Cu leads to suppression of CDW state could be related to the structural change induced by Cu doping. In TiSe$_2$, the TiSe$_2$ goes through a 2 × 2 × 2 structural transition below 200 K, leading to a CWD state.\textsuperscript{[19, 20]} The CDW state has a...

![Figure 2](image2.png)

**FIG. 2:** Temperature dependence of in-plane resistivity down to 1.8 K for $\text{Cu}_x\text{TiSe}_2$ crystals with different Cu contents. The low temperature $\rho(T)$ data are plotted in the inset.
close relationship with the structure of TiSe$_2$. When Cu is intercalated into the TiSe$_2$ layers, such 2×2×2 lattice is destroyed. The disorder of the Cu atoms destroys the superlattice of TiSe$_2$, leading to suppression of the CDW state.

![Temperature dependence of out-of-plane resistivity for Cu$_x$TiSe$_2$ crystals with different Cu contents.](image1)

The resistivity monotonically decreases with increasing Cu content. The residual resistivity ratio $\rho_{ab}(300K)/\rho_{ab}(5K)$ increases from $\sim$ 2 to $\sim$ 5 with increasing Cu content from 0.015 to 0.11. These results are consistent with that reported in polycrystalline sample.$^{[14]}$ In contrast to the results of polycrystalline samples, the samples with CDW state shows superconducting transition although the resistivity does not reach zero down to 1.8 K. In order to clearly show the superconducting transition, the low temperature $\rho_{ab}(T)$ data were plotted in the inset of Fig.2. The superconducting transition temperature ($T_{onset}$) is 1.92, 2.03, 2.24, 3.40, 4.13 and 3.02 K for the samples with $x=0.015$, 0.025, 0.055, 0.065, 0.08 and 0.10, respectively. It indicates that the superconductivity and CDW state coexist in the samples with slight Cu doping ($x \leq 0.025$), which is similar to the case of 2H family.$^{[1, 3, 4]}$ In CDW regime, $T_{onset}$ slightly increases with increasing Cu content, while CDW temperature decreases. It implies a competition of superconductivity and CDW state, similar to the case of 2H family. It should be pointed out that superconducting transition is not observed in the sample with $x=0.11$ with cooling the sample to 1.8 K. These results are nearly consistent with the phase diagram obtained from polycrystalline samples$^{[14]}$ except for the observation of superconducting transition for the slightly Cu-doped samples with CDW state.

Temperature dependence of out-of-plane resistivity $\rho_c$ is plotted in Fig.3(a) for the samples Cu$_x$TiSe$_2$ crystal with different Cu contents ($x=0.015$, 0.025, 0.055, 0.065 and 0.110). As shown in Fig.3(a), $\rho_c(T)$ shows similar behavior to $\rho_{ab}(T)$. $\rho_c(T)$ monotonically decreases with increasing Cu content. An obvious CDW hump can be observed in $\rho_c(T)$ for the slightly Cu-doped samples. The CDW state is suppressed by intercalation of more Cu. $\rho_c(T)$ shows $T^2$-dependent behavior for the samples without CDW state. Anisotropic $\rho_{ab}/\rho_c$ are shown in Fig.3(b) for the samples Cu$_x$TiSe$_2$ crystal with different Cu contents ($x=0.015$, 0.025, 0.055, 0.065 and 0.110). $\rho_{ab}/\rho_c$ shows a weak temperature dependence in all the samples with different Cu contents. It indicates that the charge transport mechanism is the same in $ab$-plane and along Cu$_x$TiSe$_2$. Compared to the case of TiS$_2$, the anisotropy for the samples Cu$_x$TiSe$_2$ is smaller. In the case of TiS$_2$ the resistivity-anisotropy is 1500 and 750 at 5 K and 300K, respectively.$^{[21]}$ In Cu$_x$TiSe$_2$, Se has larger radius and stronger covalence than S, so that the carriers can move more easily between the layers in Cu$_x$TiSe$_2$ than TiS$_2$. With intercalation of Cu, in-plane conductivity is strongly enhanced than $c$-axis conductivity, so that the anisotropy increases with increasing $x$ in Cu$_x$TiSe$_2$. A similar enhancement of anisotropy with increasing carrier content is observed in n-type cuprates.$^{[22]}$

Figure 4 shows temperature dependence of in-plane thermopower ($S$) for the Cu$_x$TiSe$_2$ crystals with

![Temperature dependence of in-plane thermopower for the samples Cu$_x$TiSe$_2$ with $x=0.015$, 0.065, 0.110.](image2)
Thermopower is negative in the whole temperature range. It indicates that the carrier is n-type. At room temperature, the magnitude of $S$ decreases with increasing $x$. Thermopower shows a non-monotonic temperature dependence for the sample Cu$_{0.015}$TiSe$_2$, a maximum value of $S$ appears at 150 K at which a CDW transition is observed in resistivity. It suggests that the non-monotonic T-dependence for $S$ arises from the occurrence of CDW order. For the samples without CDW state, the magnitude of $S$ monotonically decreases with decreasing temperature. All these results indicate that the metallic nature of Cu$_2$TiSe$_2$ is enhanced by the electron doping. It should be pointed out that the thermopower is anomalous large. Compared to the triangle lattice Na$_x$CoO$_2$ with large thermopower, Cu$_x$TiSe$_2$ shows a larger $S^2/\rho_{ab}$ at room temperature than Na$_x$CoO$_2$. In Cu$_{0.065}$TiSe$_2$, $S(300K) \approx 60\mu V/K$ and $\rho_{ab}(300K) \approx 0.15m\Omega cm$; while for Na$_{0.68}$CoO$_2$, $S(300K) \approx 90\mu V/K$ and $\rho_{ab}(300K) \approx 1m\Omega cm$. In this sense for thermoelectric material, Cu$_x$TiSe$_2$ have more larger anomalous thermopower than Na$_x$CoO$_2$. It deserves further investigation.

Figure 5 shows temperature dependence of the Hall coefficient ($R_H$) for the samples Cu$_x$TiSe$_2$ with $x=0.015$, 0.025, 0.065, 0.110.

Figure 6 shows $H^2$-dependence of isothermal in-plane magnetoresistance (MR) for Cu$_x$TiSe$_2$ with $x=0.015$, 0.055, 0.065 and 0.110 at 6 K, 15 K and 30 K. For the sample with $x=0.015$, the isothermal MR is positive, and shows a good $H^2$-dependent behavior at different temperatures. It implies that the isothermal MR just comes from the contribution of the Lorentz force on the carriers under magnetic field. However, the isothermal MR shows a complicated magnetic field ($H$) dependence for the samples with $x=0.065$ and 0.110. The MR is negative and increases with increasing $H$ at low magnetic field, then decreases and crosses zero at certain $H$, and independent behavior within uncertainty. It indicates characteristic of metal for the heavily Cu-doped sample. It further indicates that the T-dependent Hall coefficient arises from the CDW state. Formation of the CDW state leads to localization of some carriers, so that the conducting carriers decreases, and consequently enhances the Hall coefficient. This is why the $R_H$ increases below 200 K and 100 K for the samples with $x=0.015$ and 0.025 as shown in Fig.5.

![FIG. 5: Temperature dependence of the Hall coefficient ($R_H$) for the samples Cu$_x$TiSe$_2$ with $x=0.015$, 0.025, 0.065, 0.110.](image)

![FIG. 6: Isothermal magnetoresistance at 6 K, 15 K and 30 K for the samples Cu$_x$TiSe$_2$ with $x=0.015$, 0.055, 0.065, 0.110.](image)
positive MR increases with increasing H at high magnetic field. It indicates that the MR comes from two contributions: one negative and one positive component. As shown in Fig.6, the isothermal MR shows almost $H^2$-dependence at high H for the samples with $x=0.065$ and 0.110. It suggests that the MR is dominant by Lorentz force. In order to understand the complicated MR, the formula $\Delta \rho / \rho = -A_1^2 \ln (1 + A_2^2 H^2) + B_1^2 H^n$ is used to fit the experimental data. The first term in the formula comes from a semiempirical expression proposed by Khosla and Fischer[24] and has been used to explain the negative MR. The basis for this formula is Toyazawa’s localized-magnetic-moment model of magnetoresistance, where carriers in an impurity band are scattered by the localized spin of impurity atoms. It is found that all data can be well fitted by the formula for all samples. It indicates that the negative comes from the interaction between conducting carriers and localized magnetic moments. When Cu is intercalated into the TiSe$_2$ layers, some of non-magnetic Ti(IV) change into magnetic Ti(III), so that the interaction between conducting carriers and localized magnetic moments results in the negative contribution to MR. Therefore, the complicated $H$-dependent MR can be well understood. However, an anomalous MR is observed for the sample with $x=0.055$ compared to the observation of MR in other samples. The sample with $x=0.055$ shows negative MR in the whole H range, and the negative MR monotonically increases with increasing H. It indicates that the MR is dominant by the interaction between conducting carriers and localized magnetic moments even at high magnetic field. Such anomaly could be related to the critical point for disappearance of CDW state.

**CONCLUSION**

In conclusion, we have grown high quality of Cu$_x$TiSe$_2$ single crystals with different Cu contents from $x=0.015$ to $x=0.110$. The transport properties, anisotropic resistivity, thermoelectric power, Hall coefficient and magnetoresistivity are systematically studied. A systematic evolution of CDW state and superconducting state with Cu content is observed. It is found that the CDW state can be suppressed by the intercalation of Cu, while superconductivity is induced. Before the CDW state is completely suppressed, the CDW state and superconductivity can coexist and compete each other. The CDW state gives a strong effect on the transport properties, leading to T-dependent Hall coefficient. A anomalous large thermopower is observed, even comparable to large thermopower material Na$_x$CoO$_2$. Intercalation of Cu induces a negative MR due to the interaction between conducting carriers and localized magnetic moments.

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