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# Correlation between the Sign of Hall Coefficient and Lattice Instability in Substituted $TiSe_2$

(layer compound/Hall effect/phase transition)

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The temperature dependence of the electrical resistivity and the Hall coefficient at 290 K for single crystals of $Ti_{1-x}Hf_xSe_2$ are presented. The resistive anomaly due to lattice instability appears in the range of $0 \leq x \leq 0.35$ where the Hall coefficient is found to be positive. The sign of the Hall coefficient is changed to minus for $x \geq 0.4$. The results show that holes as carriers play a fundamental role in the lattice instability in $TiSe_2$.

## I. INTRODUCTION

The unusual changes in the electronic properties of the layered transition-metal dichalcogenides of group VB have been attributed to charge-density-wave (CDW) formation.[1] Electron-diffraction studies showed a superlattice formation[1,2] at the same temperature as that which characterizes the electronic anomaly. In these materials, incommensurate CDW's are formed, which lock in to the lattice to form commensurate CDW's with further decreasing temperature. Wilson *et al.*[1,2] showed that CDW's result from Fermi-surface-driven instabilities.

A lattice instability was also found in $TiSe_2$[3] which is a layered

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transition-metal dichalcogenide of group IVB. In this material only commensurate CDW state is formed below 202 K and an incommensurate CDW state has not been observed.[4] The energy-band-structure calculations[5] showed that $TiSe_2$ is a semimetal with holes near $\Gamma$ point in the Brillouin zone and electrons around L. To explain the different behavior shown by $TiSe_2$, a number of models have been proposed, which are (1) an electron-hole coupling from L to $\Gamma$ point by an electron-phonon interaction,[4] (2) an excitonic insulator-type mechanism,[6] (3) a pseudo Jahn-Teller effect,[7] and (4) a direct phonon-instability.[8]

In order to clarify the mechanism which is operative in $TiSe_2$, we have studied the mixed cation system $Ti_{1-x}Hf_xSe_2$.[9,10] $HfSe_2$ is also a layered transition-metal dichalcogenide of group IVB. Since it is, however, an indirect semiconductor with an energy gap of 1.13 eV,[11] the band gap in this system is expected to become positive as $x$ is increased. In a previous paper,[9] we reported measurements of the electrical properties of polycrystalline samples. Subsequently, we determined the onset temperatures ($T_c$) of superlattices formed in the system from resistivity measurements on single crystals.[10] The composition dependence of $T_c$ was interpreted as evidence for the real possibility of the mechanism (2).

In this paper, we wish to present an experimental study of the Hall coefficient at room temperature in addition to the temperature dependence of the electrical resistivity and to clarify the role of holes in the superlattice formation in $TiSe_2$.

## II. EXPERIMENTS

Starting materials were Ti metal powder (99.8 % pure), Hf metal powder (99 % pure) and Se powder (99.999 % pure). Powder samples were prepared by heating stoichiometric amounts of the elements in evacuated quartz tubes with excess Se to 600°C for 4 days. Then, the powders were ground in an agate mortar and refired with excess Se for 4 days. The powder samples were ground again and pressed into pellets. The pellets were heated to 800°C for 5 days with excess Se in evacuated quartz tubes in order to produce the essentially homogeneous samples. Single crystals were grown by iodine vapor transport procedure.[12] Charges of pellets were sealed in quartz tubes (28 cm long and 1.5 cm inside diameter) with iodine and excess Se ($\sim$1.5 mg/cm$^3$ of container volume). The transport tubes were placed in a two-zone furnance. The charge zone was heated to about 670°C and the growth zone was heated to 630°C for about one week. The produced single crystals were thin plates of 0.05–0.5 mm thickness.

The electrical resistivity $\rho$ and the Hall coefficient $R_H$ were measured on single crystals by use of Van der Pauw technique.[13] The expected accuracy of $R_H$ and $\rho$ is about 10 % due to non-uniform thickness and contact dimensions. The low temperatures were achieved by cooling the samples in the closed refrigeration system (Cryo-Mini, Osaka Oxygen Industries Co., Ltd.)[14] The temperatures were measured using a AuFe/Chromel thermocouple.

## III. EXPERIMENTAL RESULTS

Figure 1 shows the electrical resistivity perpendicular to the $c$ axis for single crystals of $Ti_{1-x}Hf_xSe_2$. The resistivity for $x=0$ (i. e. $TiSe_2$) exhibits a peak around 163 K. Di Salvo *et al.*[4] found that the appearance of the peak is associated with the formation of superlattice. We find the resistivity ratio $\rho$ (163 K)/$\rho$ (290 K)$\simeq$2.2. This value is somewhat lower than the estimate for $TiSe_2$ crystals grown at 590°C by Di Salvo *et al.*[4] Similar peaks are observed for $x<0.4$. However, the resistive anomaly is

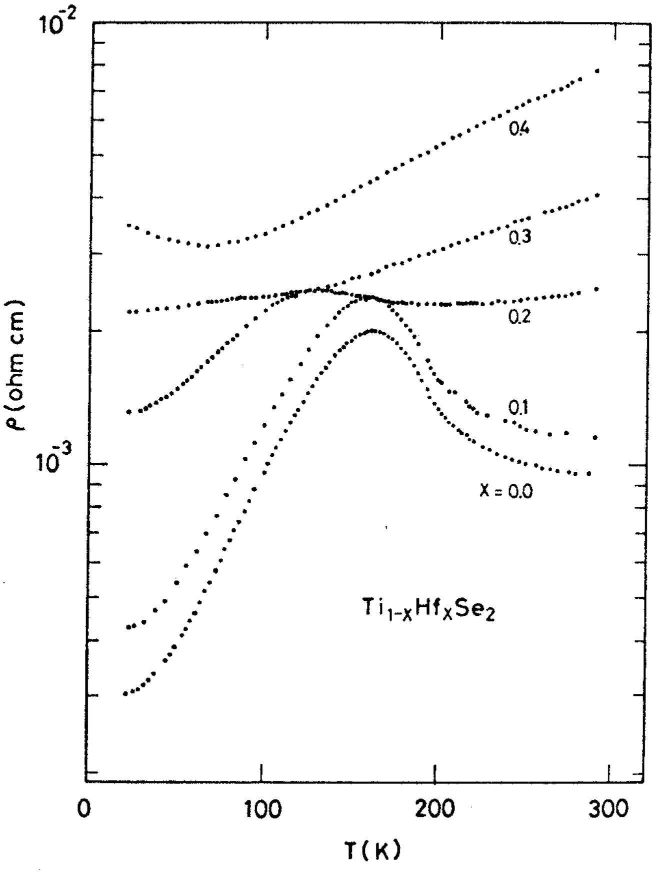

Fig. 1. Temperature dependence of the resistivity perpendicular to the $c$ axis for single crystals of $Ti_{1-x}Hf_xSe_2$.

completely suppressed for $x \geq 0.4$, where $\rho$ takes a minimum value at a low temperature. As $x$ is increased, the value of $\rho$ (290 K) increases and, at $x=0.4$, it becomes approximately an order of magnitude greater than that for $x=0$. In all the curves we find $\rho$ (22 K) $<$ $\rho$ (290 K), which is different from previous measurements on polycrystalline samples.[9]

The Hall coefficient $R_H$ (290 K) (current perpendicular and magnetic field parallel to the $c$ axis) is shown in Fig. 2. For $x=0$ (i.e. $TiSe_2$) we have determined $R_H$ (290 K)$=1.6\times10^{-2}$cm$^3$ C$^{-1}$ $\pm 10$ %. This value is in approximate agreement with that for single crystals grown at 590°C by Di Salvo *et al.*[4] Figure 2 shows that Hall coefficient on single crystals takes a positive value

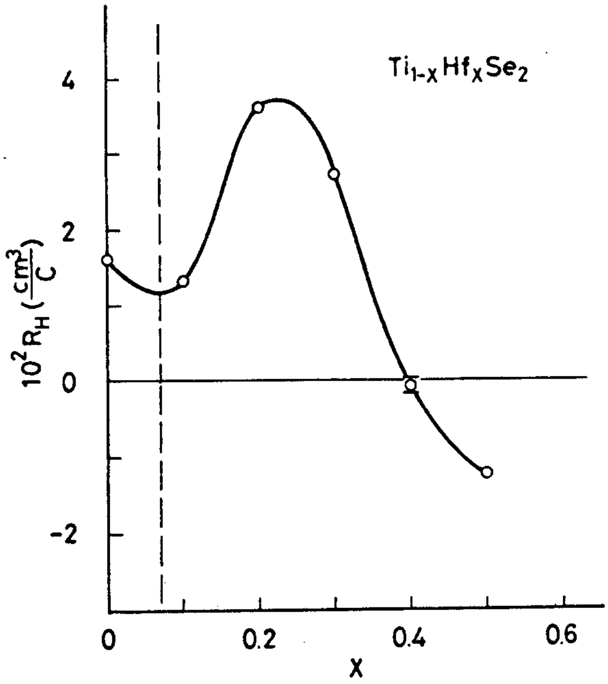

Fig. 2. Hall coefficient at 290 K vs $x$ for single crystals of $Ti_{1-x}Hf_xSe_2$. The dashed line indicates the composition where the bands are expected to first uncross.

when $0 \leq x < 0.4$. The sign of $R_H$ (290 K) is changed to minus at $x=0.4$. It should be noted that just in the above region superlattices appear. The dashed line in Fig. 2 indicates the composition where the energy gap of the system is expected to become zero.[10] In previous measurements on polycrystalline samples, the sign of $R_H$ (290 K) remains positive when $x \geq 0.4$.

## IV. DISCUSSION

As the experimental results show, the data on single crystals differ from those on polycrystalline samples. The difference cannot be fully explained at present. The following discussions are based upon the data on single crystals because, in general, single crystals are more favorable to an investigation of physical properties.

The above experimental results show positive Hall coefficient in the same region of $x$ as that where the lattice instability is observed in the system. The positive Hall coefficient means that either (1) carriers are holes, or (2) carriers are electrons and holes but mobility of holes is greater as compared with that of electrons. Since, in both cases, holes as carriers are necessary, our experiments give evidence that holes play a fundamental role in the instability. The positive sign requires many holes enough to overcome a minus Hall voltage produced by electrons. Considering that, with increasing $x$, samples tend to become dirty and excess electrons may be introduced by non-stoichiometry, impurities or defects, the number of holes is probably of the same order with that of electrons when the system exhibits superlattice for $x < 0.4$.

Let us discuss several mechanisms for the lattice instability in $TiSe_2$. White *et al.*[8] suggested that the transition is a phonon-driven antiferroelectric transition. This model gives a transition in the absence of holes contrary to the above experimental results. A band Jahn-Teller type mechanism[7] is proposed by Hughes. If the lower part of the $d_{z^2}$ band is partially populated due to non-stoichiometry, intercalation or a slight *p-d* band overlap, the opportunity exists for reducing the total energy through a distortion. In this model the presence of holes is not always the requisite for the distortion. Furthermore, it is not likely that the bands overlap near $x \simeq 0.4$ because the amount of the band overlap in $TiSe_2$ is a small quantity.[2,4,10] Among the suggested models, therefore, either (1) or (2) is considered to be the real mechanism in $TiSe_2$.

In the previous paper,[10] we have presented evidence that the excitonic insulator-type mechanism is operative in $TiSe_2$. In $Ti_{1-x}Hf_xSe_2$, the band overlap is non-existent for $x \geq 0.07$ and the size of the band gap approximately equals to the binding energy of the exciton at $x \simeq 0.35$. The origin of holes for $x \geq 0.07$ seems to be associated with fluctuations. Strong precursor effects[4)] were observed in $TiSe_2$ for about 200 K above the onset temperature of the superlattice. We interpret this phenomena as similar fluctuations with those observed in superconducting transition.[15)] For $0.07 \leq x \leq 0.35$ where the band gap opens up, this system is unstable against the formation of electron-hole pairs[16)] and the creation and the destruction of pairs may be repeated above the onset temperature of superlattice. The holes which are produced by the fluctuations possibly give a time-averaged, positive Hall voltage.

In conclusion, we have presented the experimental study of the temperature dependence of the electrical resistivity and the Hall coefficient at room temperature for single crystals of $Ti_{1-x}Hf_xSe_2$. It has been found that the sign of Hall coefficient is positive for the system where the superlattice instability arises. This indicates that the instability in $TiSe_2$ is closely correlated with the existence of holes.

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