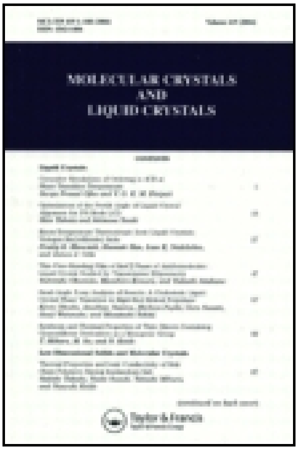

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Strong Resistivity Anomaly in a New Low-Dimensional Conductor $HfTe_5$

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STRONG RESISTIVITY ANOMALY IN A NEW LOW-DIMENSIONAL CONDUCTOR $HfTe_5$

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Temperature dependence of the resistivity, Hall coefficient and magnetic susceptibility of $HfTe_5$ with 1.5 wt. % Zr is reported. Anisotropic large diamagnetism is reported and has the peak in the vicinity of 76 K. Temperature dependence of Hall coefficient under 117 kOe clearly shows the destruction of Fermi surface at about 90 K. $HfTe_5$ can be considered to be a semimetal and observed resistivity anomaly may be accompanied by the CDW formation along c-axis. We also discuss the mixed crystal effect with $ZrTe_5$ and present the data of quantum oscillation observed at low temperature.

INTRODUCTION

In the last half decade many investigations have been done for the CDW dynamics and/or the superconductivity in transition-metal trichalcogenide compound such as $NbSe_3$. $HfTe_5$ is one of the transition-metal pentachalcogenide and crystallizes with the type A $ZrSe_3$ chain structure.[1] We observed that $HfTe_5$ exhibits a peak of the resistivity in the vicinity of 76 K.[2] Recently we have reported that Hall coefficient changes sign from positive to negative in the vicinity of 76 K.[3] And we have suggested that the above results originate from the CDW formation or some other kind of phase transition. Wieting et al.[4] and Okada et al.[5] have reported that $ZrTe_5$ shows a large peak in the resistivity near 150 K. And very recently DiSalvo et al.[6] have reported the electrical and magnetic properties of $ZrTe_5$, $HfTe_5$ and some related alloys and X-ray diffraction of $ZrTe_5$ and $HfTe_5$. In this paper we review the data of the resistivity and Hall coefficient. We report the measurement of the magnetic susceptibility, mixed crystal effect with $ZrTe_5$, and also present the data of quantum oscillation observed in the resistivity and Hall coefficient under the strong magnetic field up to 117 kOe.

EXPERIMENTAL RESULTS AND DISCUSSION

Single crystals of $HfTe_5$ were obtained by an iodine vapour transport method after Furuseth et al.[7] A temperature gradient of 500°C to 400°C was used and crystals grew in the cooler zone. The crystals of $HfTe_5$ and/or $Hf_xZr_{1-x}Te_5$ ($0<x<1$) were obtained together with single crystals with Te which often contained less than a percent of Hf. But two regions where the pentatelluride and tellurium crystallize were clearly divided in the quartz ampoule.

Each crystal was analysed by an inductively coupled plasma optical emission spectrometer (ICPOES, Jarrel-Ash Model 975). Untill now composition of Hf, Zr and Te in crystals has been determined uniquely in the same batch.

For the measurement of the resistivity and Hall coefficient the current flow was parallel to the a-axis.

(a) Resistivity and Hall coefficient

Figure 1 shows the temperature dependence of the d.c. resistivity and Hall coefficient at 1.7 kOe in $HfTe_5$ with 1.5 wt. % Zr. Strong resistivity anomaly was observed in the vicinity of 76 K. Below about 200 K the resistivity increases with decreasing temperature whereas below 76 K the conduction is metallic. Overall temperature dependence of the resistivity is quite similar to that of $TiSe_2$ which is a semimetal with p-d-bands overlap and shows $2\times2\times2$ superlattice below 200 K clearly.[8,9] No sharp structure in $d\rho/dT$ was observed as was reported by DiSalvo et al.[6] The Hall coefficient changes its sign from positive to negative at the temperature (T_p) at which the peak of the resistivity has been observed.

Temperature dependence of the resistivity below T_p was fairly different from that obtained by DiSalvo et al.[P] Their resistivity is relatively higher below T_p than that above T_p. As shown in subsection (d), the difference between our resistivity data and the data by DiSalvo et al. may be explained by using an assumption of the nonstoichiometry in the samples obtained by DiSalvo et al.

What is the mechanism of such an anomalous transport in $HfTe_5$ and/or $ZrTe_5$? When we assume that the above

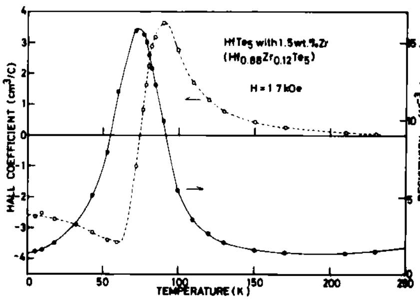

FIGURE 1 Resistivity and Hall coefficient under 1.7 kOe (sample 1).

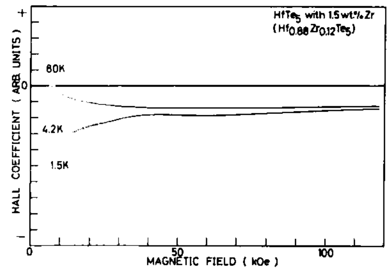

FIGURE 2 Magnetic field dependence of Hall coefficient (sample 2).

results originate from phase transition with CDW formation, observed resistivity anomaly is attributed to the superlattice formation along c-axis since DiSalvo et al. have already observed that the actual unit cell is doubled along a- and b-axes at 300 K in both $HfTe_5$ and $ZrTe_5$. They have not observed any change in the diffraction pattern above 80 K in $ZrTe_5$.[6]

Considering the above results and the magnetic field dependence of the Hall coefficient at several fixed temperature (see Fig. 3 of Ref. 3), we propose a simple two-band model.[10] In this model holes should have slightly higher mobility than that of electrons and above 200 K the number of holes are dominant. Then Hall coefficient is positive in weak field region above T_p. But below 200 K hole-like Fermi surface is destroyed and the gap is created by CDW formation with reducing the number of holes.

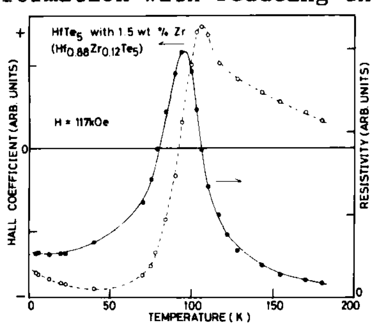

FIGURE 3 Temperature dependence of the resistivity and Hall coefficient under 117 kOe (sample 2).

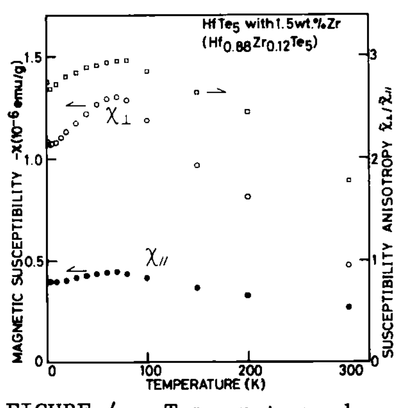

FIGURE 4 Temperature dependence of the magnetic susceptibility.

As is well known the high field limit value of Hall coefficient in the two-band model is expressed as follows:[10]

$$R_H(\infty) = -1/ec(n-p), \qquad (1)$$

where p and n are the numbers of holes and electrons, respectively. Magnetic field dependence of Hall coefficient clearly shows the saturation under strong magnetic field as is shown in Fig. 2. Figure 3 shows the temperature dependence of the Hall coefficient and the resistivity at 117 kOe. In such high magnetic field the mobility does not contribute to the Hall coefficient. Then Fig. 3 shows that the number of holes are reduced below 200 K. This result clearly shows that observed resistivity anomaly is accompanied by the destruction of the Fermi surface and majority carrier is electron at low temperature.

(b) Magnetic Susceptibility

Magnetic susceptibility above 80 K has been measured for $HfTe_5$ and $ZrTe_5$ by Furuseth et al.[7] Their data shows that observed large diamagnetism is strongly temperature dependent below 500 K in $HfTe_5$. No data at low temperature was given. Very recently DiSalvo et al.[6] have also observed magnetic susceptibility of powders of the both compounds above 4.2 K as is shown in Fig. 3 of Ref. 6. They have observed the peak of the diamagnetism at 150 K in $ZrTe_5$, but disagreement has been observed in $HfTe_5$ between T_p and the temperature at which the susceptibility has the peak. Then they concluded that the magnetic susceptibility indicated no sharp structure which relates to the resistivity anomaly and/or phase transition.

Figure 4 shows the magnetic susceptibility of the single crystals of $HfTe_5$ with 1.5 wt. % Zr ($Hf_{0.88}Zr_{0.12}Te_5$) for two configurations in which the magnetic field H is parallel to the a-axis($\chi /\!/$) and to the b-axis ($\chi\perp$). In both configurations large diamagnetic part of the susceptibility was observed and this part seems to be highly anisotropic. Observed susceptibility has the peak in the vicinity of 76 K that is T_p. This fact is quite similar to the results in $ZrTe_5$ obtained by DiSalvo et al. and in $NbSe_3$ obtained by Haen et al.[11] From our results we can conclude that observed peak of diamagnetism is strongly related to the resistivity anomaly in this compound.

When we consider the magnetic susceptibility of such a metallic compound, we can describe the susceptibility as follows:

$$\chi(T) = \chi_p^c + \chi_p^d + \chi_{vv} + \chi_{dia} + \chi_{LP} \quad (2)$$

where χ_p^c is spin-paramagnetism originating from conduction electron, χ_p^d ; spin-paramagnetism originating from d-electron, χ_{vv} ; Van Vleck paramagnetism due to d-electron, χ_{dia} ; diamagnetism due to atom core and valence electron and χ_{LP} ; Landau-Peierls(LP) diamagnetism due to conduction electron and hole. In this formula we can neglect the contributions of χ_p^d and χ_{vv} parts of paramagnetism because of our conclusion by simple chemical bonding study in our preceding paper in which it is shown that the Fermi surface is located in p-like bands.[3] As the diamagnetic part due to LP formula is large, we neglect the paramagnetic contribution of χ_p^c. χ_{dia} can be easily estimated using the following assumptions that (a) Te atom at the corner of the trigonal bicapped prism is Te^{6+},(b) Te atom of the Te chain between $HfTe_3$ chains is Te^{4+} and (c) Hf metal is Hf^{4+}. Then the total value of χ_{dia} is $- 0.098 \times 10^{-6}$ emu/g. We subtracted this value from observed $\chi_{\parallel}$ and $\chi_{\perp}$ for calculating the susceptibility anisotropy $\tilde{\chi}_{\perp}/\tilde{\chi}_{\parallel}$. The result is shown in Fig. 4. These temperature dependent and large diamagnetism has been observed in semiconductors with small energy gap and semimetals.[12] Temperature dependence of the susceptibility above 76 K may originate from the temperature dependence of the chemical potential. Of course observed large Landau-Peierls diamagnetism suggests that the mass of the carrier is small.

If we assume an ellipsoidal Fermi surface, the energy can be described as follows:

$$E(k_a,k_b,k_c) = h^2(\alpha_a k_a{}^2 + \alpha_b k_b{}^2 + \alpha_c k_c{}^2)/4\pi^2 m_e \quad (3)$$

where m_e is the mass of free electron. We can describe LP formula for $\tilde{\chi}_{\parallel}$ and $\tilde{\chi}_{\perp}$ as follows:[13]

$$\tilde{\chi}_{\parallel} \propto -m_e\mu^2((\alpha_b\alpha_c)^2/\alpha_a)^{1/3}, \quad \tilde{\chi}_{\perp} \propto -m_e\mu^2((\alpha_a\alpha_c)^2/\alpha_b)^{1/3} \quad (4)$$

where μ is a Bohr magneton. Then we get the ratio $\tilde{\chi}_{\perp}/\tilde{\chi}_{\parallel} = \alpha_a/\alpha_b$. At 1.57 K this value was estimated to be 2.8.

This fact may suggest that the electronic structure is not so highly anisotropic but also three dimensional at low temperature.

(c) Quantum Oscillations

Quantum oscillations in $NbSe_3$ have been extensively investigated by Monceau et al.[14,15] and Fleming et al.[16]

We have observed Shubnikov de-Haas effect of $HfTe_5$ with 1.5 wt. % Zr. Figure 5 clearly shows the oscillation in the transverse magnetoresistance at 4.2 K and 1.5 K. Temperature dependence of the amplitude of the oscillation is rather small. This fact suggests that the effective mass of the carrier is small. Detailed analysis of Shubnikov de-Haas effect data will be reported elsewhere.

(d) Mixed Crystal Effect with $ZrTe_5$

In mixed crystal $Hf_xZr_{1-x}Te_5$ system, the mixing ratio of Hf and Zr does not depend on the composition of powder placed in the ampoule but strongly depends on the growth temperature and/or actual temperature gradient. We have obtained the crystals $Hf_{0.88}Zr_{0.12}Te_5$, $Hf_{0.93}Zr_{0.07}Te_5$ and $Hf_{0.57}Zr_{0.43}Te_5$ in composition. The former two kinds of crystals exhibited the peak of the resistivity in the vicinity of 76 K and the last kind of crystals showed the peak about 100 K. The plot for T_p versus mixing ratio of the crystals is shown in Fig. 6 together with the data obtained by Okada et al.[5] and DiSalvo et al.[6] There are differences between our data and those obtained by DiSalvo et al.

DiSalvo et al. have emphasized that the composition is nominal and they present the composition of the powder from which crystals were grown. But they observed the peak of the resistivity of $HfTe_5$ at 50 K and T_p of $HfTe_5$ is about 70 K by means of extrapolation in Fig. 6. The T_p of the mixed crystals by DiSalvo et al. is much lower than ours. As shown in Fig. 4 of Ref. 6 the resistivity ratio below T_p is higher than that of our data (see Fig. 1 of Ref. 2).

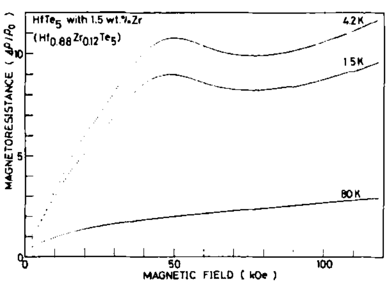

FIGURE 5 Shubnikov de-Haas oscillation in transverse magnetoresistance at 1.5 K and 4.2 K. No oscillation was observed at 80 K (sample 2). Magnetic field was parallel to the b-axis.

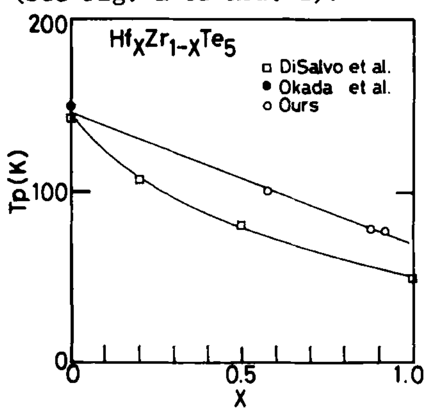

FIGURE 6 The plot for T_p versus mixing ratio in $Hf_xZr_{1-x}Te_5$

It is possible that the mixed crystals with Hf obtained by DiSalvo et al. are non-stoichiometric ones and have small amount of electrons originating from excess Hf atoms. This assumption is consistent with the following fact that their sample has small Curie contribution due to low levels of paramagnetic impurities in their magnetic susceptibility data. Perhaps this Curie contribution originates from excess Hf atoms. In our susceptibility measurement Curie contribution was not observed at low temperature. And decreasing of T_P in the resistivity data may be explained by the suppression of phase transition by cation disorder as has been shown in $TiSe_2$.[9]

The mechanism of the resistivity anomaly in $HfTe_5$ and $ZrTe_5$ should be the same.

SUMMARY AND CONCLUSION

Temperature dependence of the resistivity, Hall coefficient and magnetic susceptibility of $HfTe_5$ with 1.5 wt. % Zr was reported. Strong resistivity anomaly was observed in the vicinity of 76 K and Hall coefficient changes sign from positive to negative at T_P. Temperature dependence of the resistivity and Hall coefficient under 117 kOe showed the destruction of Fermi surface at about 90 K. To explain this phenomenon two-band model was proposed, in which we considered electrons and holes and we assumed that the destruction of Fermi surface originates from the CDW formation along c-axis because DiSalvo et al. have already observed 2×2 superlattice along a- and b-axes.

Observed semimetallic nature was confirmed by the measurement of the magnetic susceptibility and at 1.57 K we estimated the value of the ratio of the effective mass for a- and b-axes to be 2.8. Susceptibility peak was observed in the vicinity of 76 K and observed peak seems to be strongly related to the resistivity anomaly.

Qualitative consideration suggests that the suppression of phase transition may occur due to cation disorder.

Quantum oscillations, that is Shubnikov de-Haas effect was clearly observed at 4.2 K and 1.5 K for transverse magnetoresistance. Temperature dependence of the amplitude was small in this temperature range and this fact shows that the effective mass of the carrier, perhaps electron, is fairly small. $HfTe_5$ is a semimetal with small band overlap and the effective mass of the carrier is small. It is fully possible that phase transition with CDW formation along c-axis may occur in the vicinity of 76 K.

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