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THERMOELECTRIC POWER OF THE TRANSITION-METAL TETRACHALCOGENIDES: $(MX_4)_nI$

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A thermopower study has been performed on the chain compounds $(NbSe_4)_{10}I_3$, $(TaSe_4)_2I$ and $(NbSe_4)_3I$ in the range 80K-340K. The variation of thermoelectric power with temperature shows pronounced features at the Peierls transition for first two compounds and a change of slope at the displacive transition for the last one.

1. INTRODUCTION

A detailed investigation on the series of compounds $(MX_4)_nI$ is made via thermopower and electrical resistivity measurements.

All compounds which are members of this family are built with the same framework of MX_4 chains and halogen atoms between these chains. Due to their highly anisotropic structure they are candidates for CDW transport phenomena. $(TaSe_4)_2I$ and $(NbSe_4)_{10}I_3$ undergo a Peierls transition at 263 K and 280 K respectively, while $(NbSe_4)_3I$ exhibits different structural phase transitions[1].

The thermopower (TEP) is very sensitive to any changes in electronic states of conducting materials and, at present, TEP measurements have been made for almost all linear-chain compounds, except the present MX_4 family.

2. EXPERIMENTAL

The thermopower was measured using a standard temperature gradient technique. The sample was mounted on two small electrically isolated copper thermal reservoirs. Electrical connections to the sample were made via annealed gold leads attached to its ends using gold paint. The temperature gradient on the sample was measured by means of a differential Au (0.03% Fe) - chromel thermocouple with junctions glued by GE varnish as close as possible to the electrical connection for measuring the TEP. At each temperature we reversed the thermal gradient several times keeping it lower than 1K. The experimental setup was cnecked by measuring a piece of lead wire (Pb).

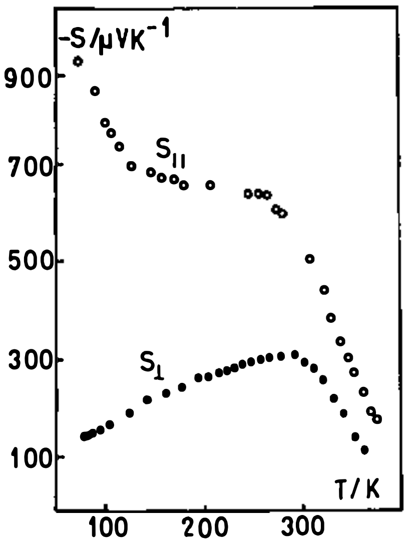

Fig.1. Thermopower of $(NbSe_4)_3I$ paralel and perpendicular to the chains versus T.

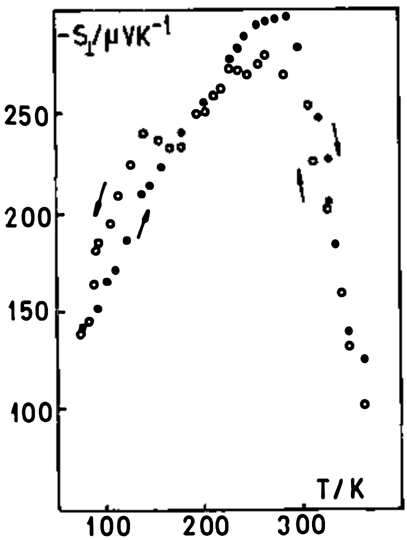

Fig.2. Thermopower of $(NbSe_4)_3I$ perpendicular to the chains during cooling o and heating •.

The TEP of $(NbSe_4)_3I$ has been measured both parallel and perpendicular to the chains (Fig.1). In the chain direction the TEP has a temperature dependence similar to that of the resistivity. Above the phase transition it has an activated form with Δ_1=4000K. Below T_p $S_{\parallel}$ is constant (650μV/K) in range between 260K and 130K and below 120K it becomes again weakly activated with Δ_2=300K. In the transverse direction TEP ($S_\perp$) is two times smaller and below T_p it decreases slightly on further cooling showing hysteresis in the heating cycle (Fig.2). The TEP is negative in both directions, what agrees well with the sign of the Hall-coefficient[2], showing that the charge carriers are predominantly electrons.

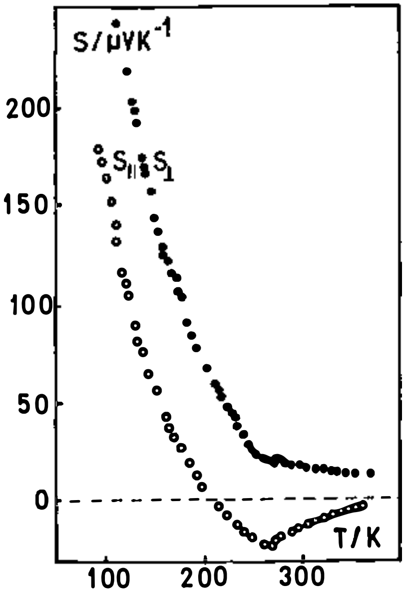

Fig.3. Thermopower of $(TaSe_4)_2I$ parallel and perpendicular to the chains.

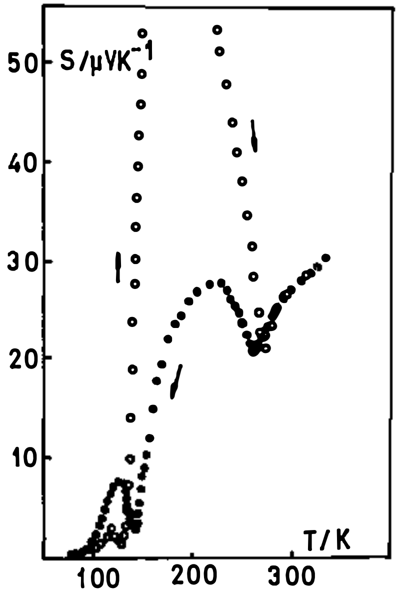

Fig.4. Thermopower of $(NbSe_4)_{10}I_3$ during cooling (●) and heating (o).

The variation of TEP with temperature for $(TaSe_4)_2I$ in both directions is shown in Fig.3. In the longitudinal direction TEP ($S_\parallel$) is slightly negative, with the minimum of $-22.5\mu VK^{-1}$ at the temperature of the Peierls transition, changing sign and increasing rapidly below this temperature. In the perpendicular direction TEP ($S_\perp$) is positive, changes slope at T_p and shows the same activated behaviour as $S_\parallel$ below T_p, in agreement the resistivity. Hall measurements also showed a change in sign corresponding to electron and hole transport above and below T_p respectively[3].

$(NbSe_4)_{10}I_3$ has positive TEP down to 80K, showing some striking features below the Peierls transition (Fig.4): a well defined minimum at T_p, a huge maximum around 200K and a smaller one at 140K. As well as the above features, the TEP displays a strong hysteretic temperature dependence below T_p. Similar, although not so pronounced behaviour, has been observed in TaS_3[5] and was attributed to conduction between the localized electronic states associated with phase solitons. This picture may also apply to our case.

It is believed that a CDW, being a condensed electronic state, has no entropy, can transport no heat and therefore produces no TEP. Therefore the variation in TEP below the Peierls transition is presumably connected with the properties of the uncondensed normal electrons.

Acknowledgement

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