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Super thermoelectric power of one-dimensional $TlInSe_2$

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Abstract

Seebeck coefficient of the structurally one-dimensional material, $TlInSe_2$, known as a p-type conductor, has been measured in the temperature range 70 °C to 500 °C in vacuum by using four probe techniques. At temperatures above 200 °C this coefficient is found to be negative. With temperature down to below 200 °C, the coefficient is becoming positive and huge to a cutting-edge value of 10^7 μV/°C. The obtained results are discussed in terms of an incommensurate superlattice phase, which might have taken place in $TlInSe_2$ at temperatures below 200 °C, and led to the above unique thermoelectric properties of this material. It is expected that thermoelectric devices based on $TlInSe_2$ will have superior parameters.

Keywords: Thermoelectric power; Seebeck coefficient; One dimensional material; Incommensurate superlattice

1. Introduction

In the past four decades thermoelectric performance of the materials and structures has attracted large interest and huge efforts have been made to rise dimensionless figure of merits ($ZT = S^2T/\rho\chi$, S-thermoelectric power or Seebeck coefficient, ρ—electric resistivity, χ—thermal conductivity, and T—temperature) above 1. Very good thermoelectric performance has been reported for Bi–Te based superlattice thin films ($ZT \sim 2.4$) [1] and layered cobalt oxide, $Ca_3Co_4O_9$ ($ZT \sim 2.7$) [2].

So far, a quantum-well approach [3,4] and a heavy-fermion scenario [5], which were suggested to put off the restrains imposed by the frames of standard one-electron picture of electronic spectrum, have been considered as most interesting and resourceful for thermoelectric device application. Meanwhile, utilization of a highly degenerate incommensurate (I) superlattice (SL) phase, which is supposed to have a multi-gaped electronic spectrum [6] with giant sensitivity to temperature and electrical field gradients, is also worthy of attention.

Novel ternary thallium compounds such as one and two dimensional (1D and 2D) $TlMeX_2$ (Me = Ga, In; X = S, Se), which have enough high melting point (>810 °C [7]) to consider their device application, have attracted our interest, because we believe that, apart from the low-dimensionality factor [3,4], a considerable increase of thermopower in these materials is also possible at the expense of I-phase that was already verified by extended X-ray examination on 1D-$TlGaTe_2$ in a wide range of temperatures [9–11].

The first data on thermoelectric power of $TlMeX_2$ appeared in 1969 in a work by Guseinov et al. [12] who reported the relatively high positive Seebeck coefficient (~800 μV/°C) for 1D-$TlInSe_2$, 1D-$TlInTe_2$ and 2D-$TlInS_2$ at temperatures above 100 °C. However, no works on the issue have appeared since then. Moreover, the angle resolved photoemission data obtained for 1D-$TlGaTe_2$ have displayed a very strong temperature dependent shift of Fermi level at temperatures below 100 °C, thus suggesting large Seebeck coefficient also at these temperatures [10]. Besides, the negative differential resistance (NDR) with a clear trend of strengthening with decreasing the temperature in the region below 100 °C has been reported for 1D-$TlInSe_2$ and 1D-$TlInTe_2$ [13].

For the above reasons, and with a thought that modern technique of thermoelectric measurements may be some-

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what advantageous over the one used 35 years ago, we have decided to return to the thermoelectric properties of $TlMeX_2$.

In this work we report the first observation of the unusual temperature behavior and giant values of thermopower of 1D-$TlInSe_2$, which was readily available, and for which band structure calculations were recently performed [14].

2. Experimental details and other relevant information

The ingot of $TlInSe_2$ we have got was obtained by Bridgmen-Stockbarger method used previously [12]. The ingot was cleaved and the samples suitable for thermoelectric measurements were then sorted out. Fig. 1 demonstrates these samples.

To an extent given by our standard X-ray examination at room temperature, all the samples looked like single crystals of $TlInSe_2$ with the space group, D_{4h}^{18}, reported previously for this material by Muller et al. [7]. However, more extended studies would have been necessary to say whether the room temperature phase of $TlInSe_2$ we examined was already incommensurately distorted. A fresh example is $TlGaTe_2$ for which only extended X-ray examination supported by calorimetric measurements disclosed the presence of I-modulation [11].

1D crystal structure of $TlInSe_2$ is shown in Fig. 2. The structure can be formally described as a set of the $(In^{3+}Se_2^{2-})^{-1}$ chains extended along the crystallographic c-axis and connected with each other through monovalent Tl^{1+} ions. At the same time, NMR studies [15] have shown that, in fact, neither Tl nor In is acquiring the just-specified charge and that above picture of underlying chemistry is corresponding more to a 1D metallic rather than semiconducting state. Nevertheless, above formal description is commonly adopted, probably because of the fact that all 1D-$TlMeX_2$ compounds become metals under quite moderate pressures [16] and, hence, eventually match this description.

Seebeck coefficient and dc-resistivities were measured by four-probe technique [17,18] in vacuum in the temperature range 70 °C to 500 °C. Silver paste was used for contacts and carbide tangsten line for wiring. The contacts proved to be ohmic.

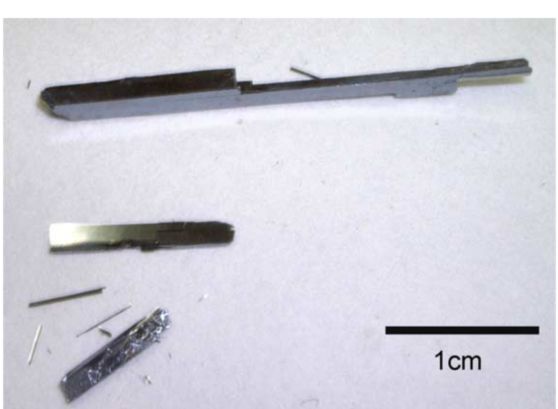

Fig. 1. Samples of $TlInSe_2$ used for thermoelectric measurements.

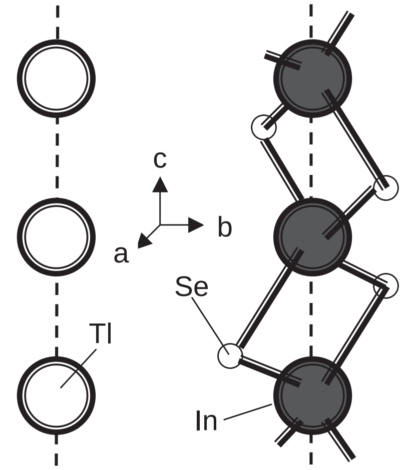

Fig. 2. Fragments of 1D-crystalline structure of $TlInSe_2$. Dashed lines show direction of chains.

The data on electrical resistivities of $TlInSe_2$ at ambient conditions were already reported to be $\rho_{II}=99.6\ \Omega$ cm and $\rho_{\perp}=24.9\times10^3\ \Omega$ cm, where ρ_{II} and $\rho_{\perp}$ are the resistivities parallel and perpendicular to the c-axis, respectively [16]. Our samples generally matched the above electrical description, but the values of resistivities turned out to be higher (by order of magnitude).

All the measurements were made on a number of samples and were reproducible to a good extent.

3. Results and discussion

In Fig. 3 we show the temperature dependence of Seebeck coefficient of $TlInSe_2$ for temperatures above 150 °C. A striking feature of this dependence is the change of the sign of this coefficient at temperatures around 200 °C.

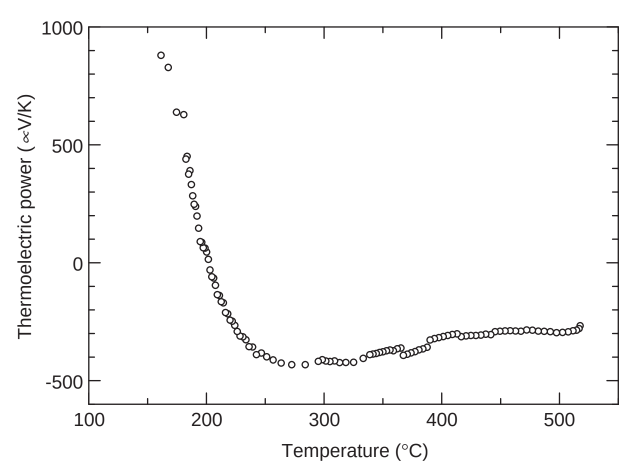

Fig. 3. Seebeck coefficient of $TlInSe_2$ as a function of temperature between 150 °C and 500 °C.