ISSN 1330–0008
CODEN FIZAE4

LETTER TO THE EDITOR

ANISOTROPIC THERMOELECTRIC PROPERTIES OF $(TaSe_4)_2I$

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Received 4 September 2000; Accepted 11 December 2000

Measurements of temperature dependence of the electrical conductivity and thermopower along the chain and perpendicular-to-chain directions of the inorganic conductor $(TaSe_4)_2I$, exhibiting the charge density wave transition, are reported. The electrical conductivity and thermopower along the chain and perpendicular-to-the chain direction were measured for the first time on the same sample. Measurements in both directions enable obtaining an information on the predominant carriers along different crystallographic directions which may be different due to different energy gaps.

PACS numbers: 72.15.N, 84.32.F, 72.20.P UDC UDC 537.12, 537.32

Keywords: quasi-one-dimensional systems, charge density waves, electrical conductivity, thermopower, anisotropy

Peierls predicted [1] that in one-dimensional systems electron-phonon coupling may cause a phase transition due to the instability of the lattice. Below the Peierls phase transition temperature, T_P, this instability modulates both the ionic position, with a wave vector $q = 2k_F$ (k_F is the Fermi wave vector) and the electronic density, generating a charge density wave (CDW). Periodicity of the CDW can be either commensurate or incommensurate to the periodicity of the underlying lattice. Peierls transitions have been found in a number of quasi-one-dimensional systems with a high anisotropy of electrical conductivity. Anisotropy ratio (i.e. the ratio between electrical conductivities measured along the chain and perpendicular to the chain direction) is typically of the order of $10^2 - 10^3$ [2].

$(TaSe_4)_2I$, the quasi-one-dimensional compound studied here, is composed of parallel $TaSe_4$ chains separated by strands of iodine atoms and exhibits an incommensurate Peierls transition at temperatures between 250 K and 260 K. The room-temperature structure of $(TaSe_4)_2I$ has a tetragonal unit cell with lattice parameters $a = 0.9531$ nm and $c = 1.2824$ nm [3]. Electronic band structure calculation [4] shows that the conduction band is built from Ta orbitals, with overlapping labels directed along the chain axis. The magnitude of the electronic gap is correlated with the dispersion in Ta-Ta bond lengths along the $(TaSe_4)$ chains.

Single crystals of $(TaSe_4)_2I$ were grown under conditions described previously [5]. The sample of $(TaSe_4)_2I$, used for the electrical conductivity and thermopower measurements, was in the shape of a rectangular prism, with dimensions 0.7 mm × 1.9 mm × 2.9 mm. Figure 1 shows a sketch of the sample geometry, and the contact configurations for the electrical conductivity measurements. In order to minimize the contact resistance, gold wires were glued to the sample with graphite paint. The thermopower measurements were made by applying a differential method with two identical thermocouples (chromel versus gold with 0.07% iron), attached to the sample with silver paint.

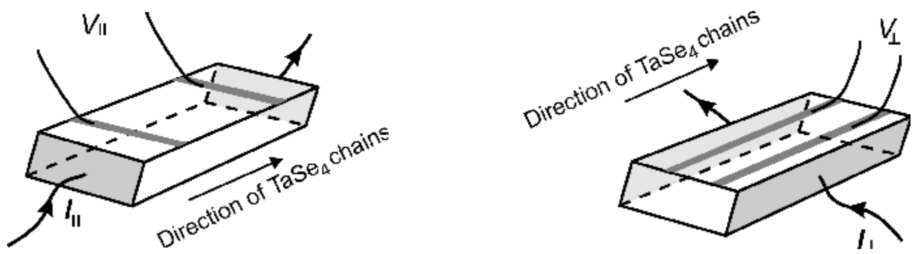

Fig.1. Sketch of the sample geometry and the contact configurations for the electrical conductivity measurements.

Temperature dependence of the electrical conductivity, $\sigma(T)$, is shown in Fig. 2. The electrical conductivities along the chain, $\sigma_{\|}(T)$, and perpendicular to the chain direction, $\sigma_{\perp}(T)$, exhibit a semiconductor behaviour in the whole temperature range. The semiconducting character of $\sigma_{\|}(T)$ above the transition temperature, T_P, suggests the existence of a pseudo gap. The temperature behaviour of $\sigma_{\perp}(T)$ is changed at T_P, resulting in a small and broad peak in negative logarithmic derivative of conductivity, $-\mathrm{d}[\ln \sigma(T)]/\mathrm{d}(1000/T)$, shown in the inset of Fig. 2. This change in $\sigma_{\perp}(T)$ at T_P is caused by the change in hopping integrals between the chains of the electron system, due to (re)modulation of Ta-Ta distances. The value of the electrical conductivity $\sigma_{\|}(T)$ at room temperatures is in agreement with the previously published data [2], while the value of $\sigma_{\perp}(T)$ is an order of magnitude lower than the previously published value [4]. Therefore, the observed anisotropy ratio, $\sigma_{\|}(T)/\sigma_{\perp}(T)$, at room temperature is an order of magnitude larger, which is more alike to the anisotropy ratios obtained in other Peierls systems [2]. The transition temperature, T_P, has been determined to be 253 K. This value is derived from the sharp peak in the negative logarithmic derivative of the electrical conductivity measured along the chain direction, $-\mathrm{d}[\ln \sigma_{\|}(T)]/\mathrm{d}(1000/T)$, (see inset of Fig. 2). The conductivities measured in both directions well bellow T_P

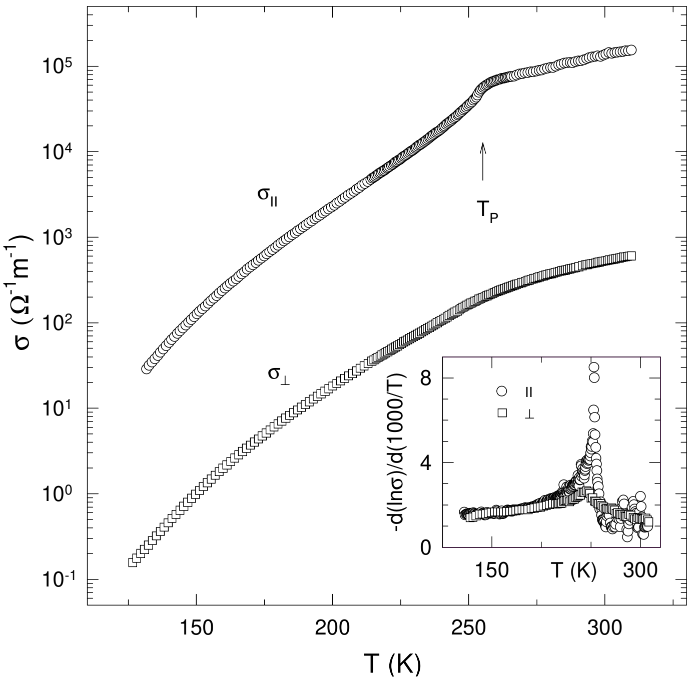

Fig. 2. Temperature dependence of the electrical conductivity, $\sigma(T)$, of $(TaSe_4)_2I$ *measured along $\sigma_{\|}(T)$, and perpendicular $\sigma_{\perp}(T)$ to the chain axis. Inset shows the negative logarithmic derivative of the electrical conductivity,* $-\mathrm{d}[\ln \sigma(T)]/\mathrm{d}(1000/T)$, *versus temperature, T. The derivative of the $\sigma_{\perp}(T)$ shows a weak temperature variation, with a broad anomaly around T_P, without a sharp singularity, as in the case of $\sigma_{\|}(T)$.*

follow the activation energy law $\sigma(T) = \sigma(0)\exp(-\Delta(T)/k_B T)$ (as can be seen from the straight lines in Fig. 3.). From such variation (and also from the plateaus in the $-\mathrm{d}[\ln \sigma(T)]/\mathrm{d}(1000/T)$ at low temperatures shown in the inset of Fig. 2.), one can deduce that the value of the low temperature energy gap ($\Delta(0) = 1580$ K) is equal in both directions. Previously obtained value of $\Delta(0)$ along the chain direction [2] is in agreement with our result. The temperature dependence of the electrical conductivity of the quasi-one-dimensional systems at electrical fields smaller than the threshold field E_T, approximately follows the relation [6]

$$\sigma(T) = \frac{C}{\Delta(T)} \exp \frac{-\Delta(T)}{k_B T} \tag{1}$$

where $\Delta(T)$ is the temperature-dependent energy gap (which is different for two different crystallographic directions), and C is a constant. By using that expression and the value of the low temperature energy gap $\Delta(0)$, the temperature dependence of the energy gaps in both directions, $\Delta_{\|}(T)$ and $\Delta_{\perp}(T)$, are estimated, and shown in the inset of Fig. 3. Below the transition temperature, T_P, $\Delta_{\|}(T)$ follows a scaled mean-field dependence [7], while above T_P, there is a pseudogap [8] due to the existence of fluctuations. An estimation of $\Delta_{\perp}(T)$ shows that in-chain phase transition had influenced an inter-chain conductivity in the sense that the energy gap changed ($\Delta_{\perp} \approx 1580$ K in the temperature range $T < T_P$, and ($\Delta_{\perp} \approx 1350$ K for $T > T_P$).

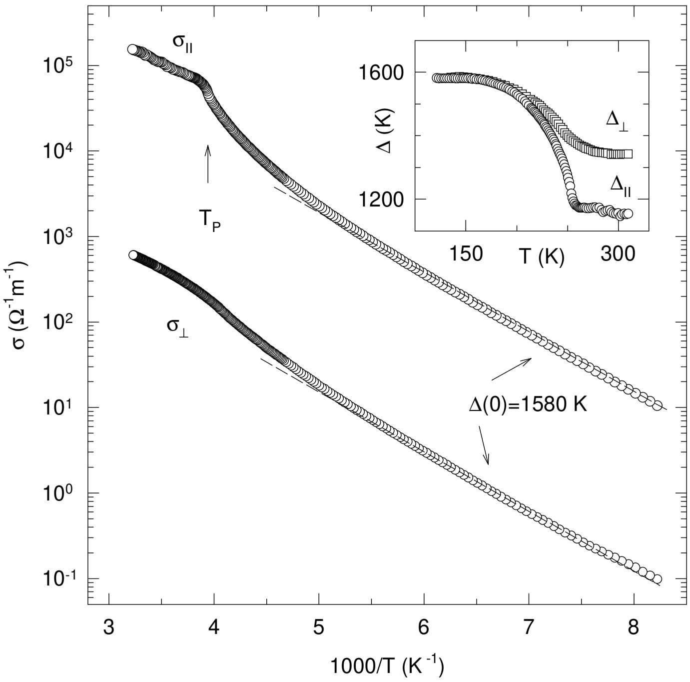

Fig. 3. Electrical conductivity, $\sigma(T)$, versus inverse temperature, $1000/T$, of $(TaSe_4)_2I$, measured along $\sigma_{\|}(T)$ and perpendicular $\sigma_{\perp}(T)$, to the chain axis. The energy gap values $\Delta(0)$ are evaluated from the dashed lines in the figure. The inset shows the temperature dependence of the energy gap $\Delta(T)$ derived from the electrical conductivity data $\sigma_{\|}(T)$ and $\sigma_{\perp}(T)$ using Eq.(1).

The temperature dependence of the thermopower measured along the chain direction, $S_{\|}(T)$, and in the direction perpendicular to the chains, $S_{\perp}(T)$, are shown in Fig. 4. The anisotropy is striking. In the vicinity of the transition temperature, the signs of the thermopower are opposite, and their temperature dependence is different. The thermopower measured along the chain direction, $S_{\|}(T)$, exhibits metal-like behaviour for temperatures $T > T_P$, and semiconductor behaviour for $T < T_P$. Change of the sign of the thermopower is related to the change from the electron to the hole-like conductivity, as seen in the Hall coefficient measurements [9]. The thermopower in the perpendicular-to-chain direction, $S_\perp(T)$, shows a semiconductor behaviour in the whole temperature range, with a change of slope at T_P. The temperature behaviour of the thermopower is in agreement with the previously published data on $S_\parallel(T)$ and $S_\perp(T)$, obtained on two different samples [10].

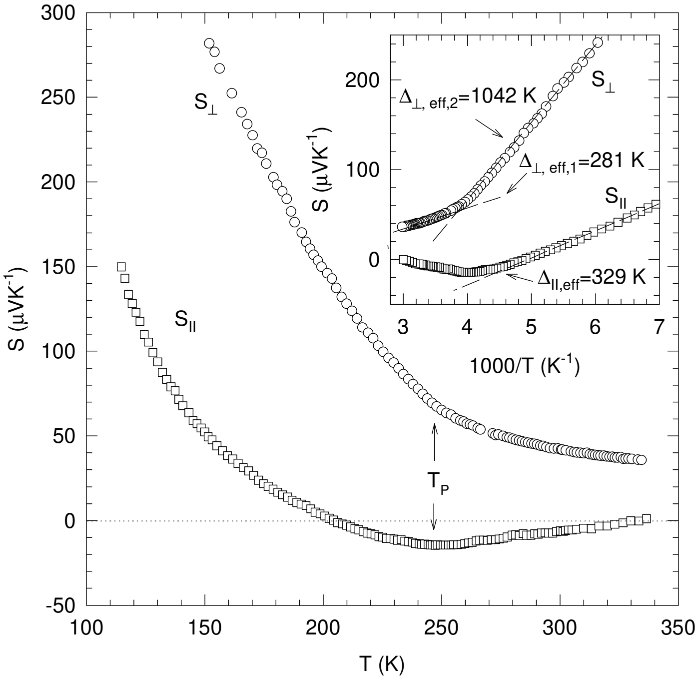

Fig. 4. Temperature dependence of thermopower, $S(T)$, of $(TaSe_4)_2I$ in the chain direction ($S_\parallel(T)$) and in the direction perpendicular to the chains ($S_\perp(T)$). The inset shows thermopower $S_\parallel(T)$ and $S_\perp(T)$ as a function of inverse temperature, ($1000/T$). Values of the effective energy gap are estimated from the linear behaviour at temperatures below the transition temperature, T_P, for the chain direction, and two linear fits at $T > T_P$ and $T < T_P$ for the perpendicular-to-chains direction.

For an uncorrelated degenerate Fermi gas, the thermopower $S(T)$ can be derived from the Boltzmann equation [11], and for the free electrons in metals, thermopower varies linearly with temperature

$$S(T) = -\frac{\pi^2 k_B^2}{eE_F}\, T\,, \tag{2}$$

where E_F is the Fermi energy. Although the thermopower measured along the chains in $(TaSe_4)_2I$ shows a linear temperature dependence for $T > T_P$, the Fermi energy E_F can not be derived from this measurement due to the fact that the temperature range is relatively restricted, and, furthermore, the electrical conductivity data showed nonmetallic behaviour at $T > T_P$. Semiconductor theory can be used to explain the thermopower results in the temperature range below T_P. For intrinsic semiconductors, the following equation is valid [12]

$$S(T) = \frac{1-b}{1+b}\,\frac{\Delta(0)}{ek_B}\,\frac{1}{T} + const = \Delta_{\mathrm{eff}}\,\frac{1}{T} + const\,, \tag{3}$$

where b is the electron to hole mobility ratio ($b = \mu_e/\mu_h$), $\Delta(0)$ the low-temperature energy gap and Δ_{eff} is the effective energy gap. The constant in Eq. 3 depends on the distribution of charge carriers in the conduction and valence bands. The thermopower data shown in Fig. 4 have been redrawn in the inset of Fig. 4 as a function of the inverse temperature, $1/T$. In the temperature range below T_P, the effective energy gap along the chain direction can be calculated, and its value is: $\Delta_{\parallel,\mathrm{eff}} = 329$ K. By using the value of the energy gap, $\Delta(0)$, calculated from the electrical conductivity measurements ($\Delta(0) = 1580$ K), the electron to hole mobility ratio, b, can be deduced, as well. Its value is equal to 0.66, which shows that holes along the chain direction exhibit a greater mobility compared to electrons, as already noticed in Ref. [13]. By fitting the data of the thermopower measured in the perpendicular-to-chain direction, and using Eq. (3), we get the effective gap

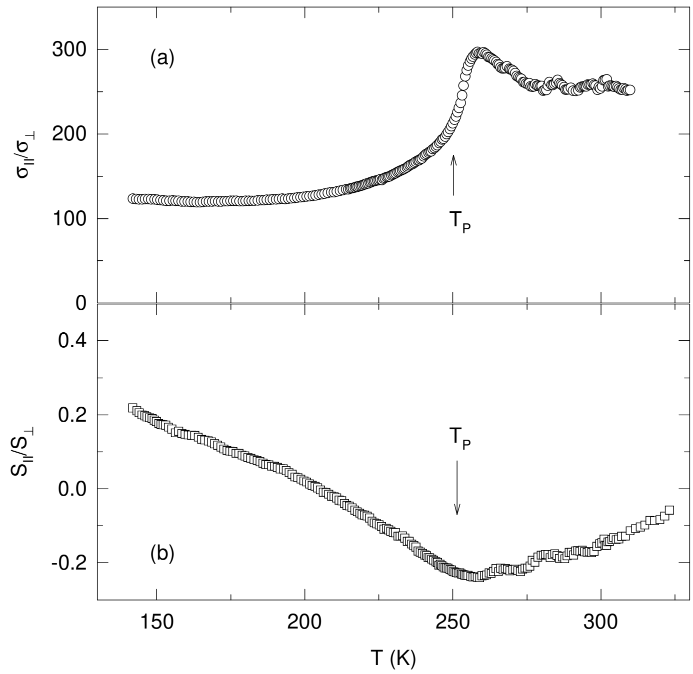

Fig. 5. Anisotropy of the electrical conductivity: a) $\sigma_\parallel/\sigma_\perp$ and (b) thermopower $S_\parallel/S_\perp$, of $(\mathrm{TaSe_4})_2\mathrm{I}$ as a function of temperature, T.

$\Delta_{\perp,\mathrm{eff},2} = 1042$ K bellow, and $\Delta_{\perp,\mathrm{eff},1} = 281$ K above the transition temperature T_P. The corresponding mobility ratios b are 0.21 and 0.70, respectively.

The temperature dependence of the anisotropy ratios, $\sigma_{\parallel}/\sigma_{\perp}$ and $S_{\parallel}/S_{\perp}$, are shown in Fig. 5. As seen, in contrast to the conductivity ratio (Fig. 5.a), the anisotropy of thermopower (Fig. 5.b) exhibits the opposite temperature behaviour in the temperature range above and below T_P. The anisotropy of the transport properties in this system is probably due to the highly anisotropic band structure and phonon drag effects.

In summary, we have demonstrated that the Peierls transition, which occurs at 253 K, affects the electrical conductivity and thermopower of $(\mathrm{TaSe}_4)_2\mathrm{I}$ along the chain and perpendicular-to-chain directions. The band structure anisotropy causes the strong anisotropy of electron transport properties: a) electrical conductivity is two orders of magnitude larger along the chain than in the perpendicular-to-chain direction; b) the magnitude of thermopower in both of investigated directions is significantly different in a broad temperature range, and of opposite sign in the vicinity of the Peierls transition.

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ANIZOTROPNA TERMOELEKTRIČNA SVOJSTVA $(TaSe_4)_2I$

Načinili smo mjerenja temperaturne ovisnosti električne vodljivosti i termostruje uzduž i poprečno na smjer lanaca neorganskog vodiča $(TaSe_4)_2I$ koji pokazuje prijelaz na valove nabojne gustoće. Ovo su prva mjerenja električne vodljivosti i termostruje uzduž i poprečno na smjer lanaca na istom uzorku. Mjerenja u oba smjera omogućuju dobivanje podataka o nositeljima naboja duž dviju kristalografskih osi koji mogu biti uzrokovani različitim energijskim procjepima.