# Investigation of metal–semimetal phase transition in $(TSeT)_2Cl$

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We have studied the behavior of the magnetoresistance and of the conductivity anisotropy of the complex $(TSeT)_2Cl$ at temperatures in the region of the phase transition. The magnetoresistance above 17 K is isotropic and an analysis of its behavior shows that it is due principally to a shift of the transition point under the influence of the magnetic field. The relative change of the transition temperature in this region has a quadratic field dependence and amounts to 3% in a field of 50 kOe. A noticeable transverse magnetoresistance of the ordinary type appears below the transition temperature. Order-of-magnitude estimates show that the carrier density decreases in this case by one or two orders.

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## INTRODUCTION

The main properties of the quasi-one-dimensional organic metal $(TSeT)_2Cl$ were described in Refs. 1 and 2. The crystal structure of this compound is typically quasi-one-dimensional and is characterized by the presence of stacks of TSeT molecules stretched out along the $c$ axis. The room-temperature conductivity along this direction is $2.1\times10^3\ \Omega^{-1}\cdot cm^{-1}$ and increases when the temperature is lowered all the way to 26–27 K; the magnetic susceptibility is practically independent of temperature in this interval. All this attests to the metallic character of the electronic state of the complex, and, assuming the band to be one-dimensional and cosinusoidal, it is possible to estimate from the susceptibility[1)] the Fermi velocity $v_F=3.4\times10^6$ cm/sec and the band width $\Delta E=1.2$ eV.

Below 27 K, a transition to a new state sets in and is characterized as $T\to0$ by a finite conductivity of the order of the room-temperature value and a finite value of the paramagnetic part of the susceptibility.

We describe here an attempt at a more detailed investigation of the nature of this transition. We present the results of measurements of the magnetoresistance of $(TSeT)_2Cl$ and of the anisotropy of its conductivity; these results show that the temperature of the aforementioned transition decreases under the influence of the magnetic field and that the low-temperature state is characterized by a small number of carriers and that although it is strongly anisotropic it is not quasi-one-dimensional.

## MEASUREMENT RESULTS

We used for the measurements single cyrstals with characteristic transverse dimensions of about 50 $\mu$m and length up to 3 mm. The details of their synthesis are described in Ref. 3. The magnetoresistance was measured in the temperature interval from 1.5 to 42 K and in fields up to 55 kOe with the magnetic field oriented along and across the current direction, which always coincided with the $c$ axis. The anisotropy of the conductivity was measured by Montgomery's method[4] in the interval from room temperature to 4.2 K. The contacts were connected to the side faces of the crystal opposite each other, and the distance between two pairs ranged from 0.3 to 1 mm.

Figure 1 shows the temperature dependence of the relative resistivity change $\rho=[R(H)-R(0)]/R(0)$ in a 50-kOe field for several single crystals. Above the temperature of the maximum conductivity, the value of $\rho$ is positive and isotropic. When the temperature is lowered, $\rho$ reverses sign, goes through zero at 26 K, and reaches a maximum negative value at 17 K. At lower temperature the magnetoresistance becomes noticeably anisotropic.

In the temperature region where the magnetoresistance is isotropic, it has a quadratic dependence on the applied field (Figs. 2 and 3). At low temperatures the field dependence of $\rho$ is more complicated (Fig. 4). Whereas $\rho_\perp$ becomes a linear function in fields stronger than 20 kOe, $\rho_\parallel$ exhibits some tendency to saturation.

A typical plot of the conductivity anisotropy against temperature is shown in Fig. 5. At room temperatures the measured 8 crystals had $\sigma_\parallel/\sigma_\perp=60\pm20$, and the transverse conductivity was independent of the orientation of the crystal with the same degree of accuracy. The large scatter is due mainly to the error in the determination of the distances between the contacts, while the accuracy with which the temperature dependences of the anisotropy of the various crystals were measured could be lower by one order of magnitude.

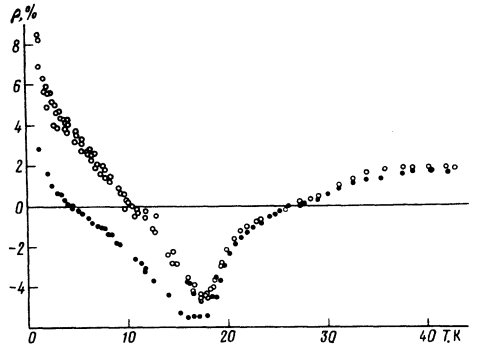


FIG. 1. Temperature dependence of the relative change of the resistance in a field 50 kOe; ○—$H\perp J$; ●—$H\parallel J$. The data are for several single crystals.

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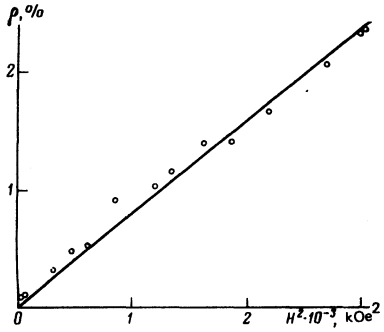


FIG. 2. Dependence of the magnetoresistance on the field at $T=40$ K.

With decreasing temperature, the anisotropy of the conductivity increases and reaches a maximum near 30 K, where both conductivities also go through a maximum. With further decrease of temperature, the anisotropy decreases, owing to the stronger decrease of $\sigma_{\parallel}$ than that of $\sigma_{\perp}$.

## DISCUSSION

The isotropic character of the magnetoresistance at temperatures higher than 17 K indicates clearly that the influence of the magnetic field on the resistance is exerted in this temperature region via the spin system and is not connected with the ordinary galvanomagnetic effects due to the Lorentz force. Two mechanisms can be indicated for this influence. One of them is due to the field-induced shift of the phase-transition temperature $T_c$, and the other is due to the change in the character of the scattering on account of the partial polarization of the spins.

It can be assumed that the shift of the transition temperature will lead simply to a change in the temperature scale, and if in the absence of a field the sample resistance $R_0$ in the vicinity of the transition is a certain function of the $\varkappa$ ratio $T/T_c$

$$R_0=R(T/T_c),$$

the resistance $R_H$ in a magnetic field can be represented in the form

$$R_H=R(T/T_{cH})+\delta R,$$

where $T_{cH}=T_c-\Delta T_c$ is the transition temperature in the field $H$, and $\delta R$ is the resistance increase due to

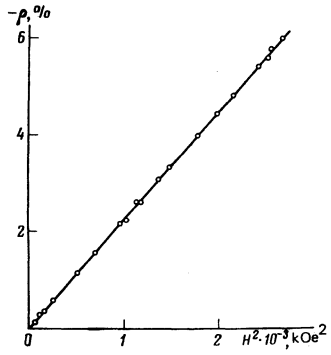


FIG. 3. Dependence of the magnetoresistance on the field at $T=17$ K.

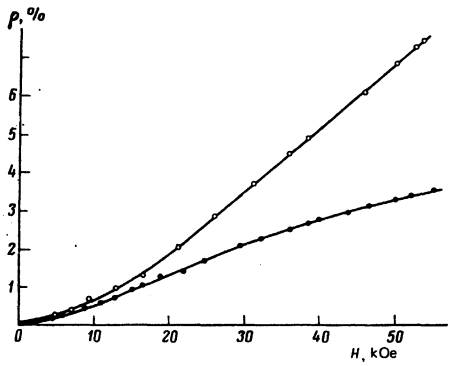


FIG. 4. Dependence of the magnetoresistance on the field at $T=1.4$ K: ○—$\mathbf{H}\perp\mathbf{J}$; ●—$\mathbf{H}\parallel\mathbf{J}$.

the additional contribution to the scattering. Hence

$$\rho=\frac{\Delta R}{R_0}=\frac{T}{R_0}\frac{\Delta T_c}{T_c}\frac{\partial R}{\partial T}+\frac{\delta R}{R_0},$$

and it is seen that this description agrees qualitatively with the observed behavior of $\rho$ (Fig. 1), which reverses sign together with the derivative $\partial R/\partial T$ and vanished near the temperature of the maximum conductivity. It follows also that $\delta R$ is small.

The smallness of $\delta R$ makes it possible to determine $\Delta T_c/T_c$ from the temperature shift between the $R_0(T)$ and $R_H(T)$ curves. A given resistance is obtained in a magnetic field at a lower temperature than in the absence of a field, and the corresponding temperature difference can be determined either experimentally or from the relation

$$R_H(T-\Delta T)=R_0(T),$$

which yields

$$\Delta T=\frac{\Delta T_c}{T_c}T+\frac{\delta R}{\partial R/\partial T}.$$

The experimental dependence of the shift $\Delta T$ on the temperature is shown in Fig. 6 for two single crystals in a 50-kOe field parallel to the current. It is seen that the experimental points are indeed grouped on both sides of the line $\Delta T=(\Delta T_c/T_c)T$ in accord with the sign of the derivative $\partial R/\partial T$. The line shown in the figure corresponds to a relative transition-temperature decreases $\Delta T_c/T_c=3\%$.

It is seen from Figs. 2 and 3 that $\rho$ is proportional to $H^2$ in the considered temperature region. It follows therefore from the foregoing discussion that we can

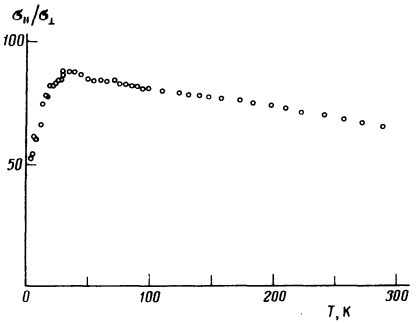


FIG. 5. Dependence of conductivity anisotropy on the temperature.

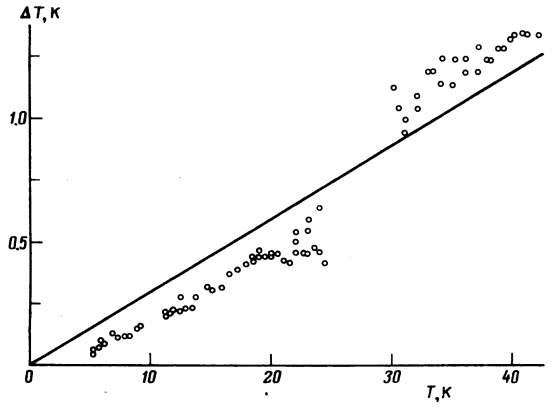


FIG. 6. Dependence of the temperature shift between the $R_0(T)$ and $R_H(T)$ curves in a field of 50 kOe parallel to the current. Dat for two single crystals.

write

$$\Delta T_c/T_c=\alpha(\mu H/kT_c)^2,$$

and if the characteristic temperature is taken to be $T_c = 17$ K, we get $\alpha = 0.77$. This is approximately 4 times larger than obtained for the shift of the Peierls transition in a magnetic field.[5]

In our case the low-temperature state of the complex is not dielectric, so that the phase transition in question cannot be regarded as a pure Peierls transition. One of the possible causes of the preservation of the metallic state below the transition temperature, as indicated in Ref. 2, may be the splitting of the initial fourfold degenerate conduction band into several subbands. Another cause may be three-dimensional effect that cause corrugation of the initially flat Fermi surface and violation of the condition $\varepsilon(\mathbf{q}) = -\varepsilon(\mathbf{q}+\mathbf{q}_0)$ on part of this surface. As a result, electron or hole pockets are formed on the Fermi surface after the transition, and the substance remains a semimetal.

The behavior of the complex indicates clearly a significant role of three-dimensional effects at low temperatures, when the conductivity anisotropy decreases and the magnetoresistance becomes noticeably anisotropic. It can be concluded from Fig. 6 that the longitudinal magnetoresistance continues to be due mainly to a shift of the transition point down to temperatures on the order of several degrees. The additional contribution to the transverse magnetoresistance can therefore now be attributed to ordinary galvanomagnetic effects. This shows that ordinary kinetics comes into play at low temperatures, and we can roughly estimated the carrier density $n$ in the low-temperature phase by using the simplest relations

$$\rho_\perp-\rho_\parallel\sim(\omega\tau)^2, \quad \omega\tau\sim Hc^{-1}(\mu_\parallel\mu_\perp)^{1/2}, \quad \sigma_\parallel\sigma_\perp\sim(ne)^2\mu_\parallel\mu_\perp,$$

where $\mu_\parallel$ and $\mu_\perp$ are respectively the longitudinal and transverse mobilities. This yields

$$n\sim\frac{H}{ec}\left(\frac{\sigma_\parallel\sigma_\perp}{\rho_\perp-\rho_\parallel}\right)^{1/2}$$

and assuming $\sigma_\parallel\sim 10^4\ \Omega^{-1}\cdot\mathrm{cm}^{-1}$, $\sigma_\perp\sim 10^2\ \Omega^{-1}\cdot\mathrm{cm}^{-1}$ and $\rho_\perp-\rho_\parallel\sim 0.01$ in a field 50 kOe we get $n\sim 3\times10^{19}\ \mathrm{cm}^{-3}$, smaller by a factor of 30 than the initial electron density in the complex.

Our discussion shows thus that the phase transition in the $(TSeT)_2Cl$, which occurs near 20 K, is more likely a transition from the metallic into the semimetallic state. Two circumstances seem not quite usual in this case. If the foregoing treatment of the magnetoresistance is correct and its onset in the high-temperature region is indeed due to a shift of the transition point under the influence of the magnetic field, then it is seen, first, that the influence of the latter manifests itself already at temperature more than double the transition temperature, and second, that the shift of the transition temperature is several times larger than would follow from the simple theory,[5] although one might expect that various factors not accounted for in this theory would more readily lead to a weakening of the effect.

[1)]We take the opportunity to note that the values given in Ref. 7 for these quantities are half the correct ones.

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