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Indications of Charge Density Wave Formation in the Quasi One-Dimensional Compound TiS_3

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Nonlinear transport phenomena associated with the depinning and sliding of charge density wave (CDW), have been observed approximately in ten inorganic quasi –one-dimensional compounds. Most of them are tri- or tetrachalcogenides of Group V transition metals [1].

Titanium trisulfide TiS_3 is a member of another interesting class of compounds – triachalcogenides of Group IV transition metals. These layered quasi one-dimensional compounds crystallize monoclinically. Linear chains of metal atoms are parallel to the *b* axis. The chains form layers in the *ab* plane, which are isolated from each other by double layers of sulfur atoms and are coupled with each other by the van der Waals interaction [2]. The materials are diamagnetic semiconductors, with exception of $ZrTe_3$ and TiS_3 showing metallic properties. At high temperatures the resistance of TiS_3 in the direction of the conducting chains decreases with decrease in the temperature. A minimum on the temperature dependence of the resistance, *R(T)*, is observed near 250 K, where a crossover from the metallic to the dielectric behavior occurs [3,4]. Below 200 K *R* starts to depend on frequency [3]. The behavior could be attributed to the CDW formation. However, neither structural evidences for the periodic lattice distortion, nor nonlinear conductivity have been found [3,4]. The dielectric behavior of TiS_3, as well as the frequency dependence of the resistance below 200 K, was explained by localization effects [3].

Until recently TiS_3 has been studied only at temperatures higher than 40 K. Here we report the dependences of conductivity of TiS_3 on *T* and electric field *E* down to liquid helium temperatures. Nonlinear conduction and indications of phase transitions are found.

The TiS_3 whiskers are ribbon-like single crystals with dimensions of (500–3000)×(10–200)×(1–20) μm^3 along the *b*, *a*, and *c* directions, respectively. Studies of thin semitransparent samples in the *ab* plane by transmission electron microscope at 300 and 155 K showed high quality of the crystals and confirmed the absence of the Peierls transition in this temperature range, in agreement with [3,4].

The temperature dependences of resistance along the chains (*b* axis), $R_{\|}$, and across the chains (*a* axis), $R_{\perp}$, were measured from 340 to 4.2 K. Fig. 1 shows the corresponding curves in the range 4.2 K<*T*<300 K. The longitudinal resistivity measured at *T* = 300 K is $\rho_{300} \approx 2\ \Omega$cm, which is in agreement with the results reported in [3]. The *a*-axis resistivity at room temperature is about five times higher. The relatively small anisotropy of the resistivity $\rho_a/\rho_b \approx 5$ at *T* = 300 K increases by two orders of magnitude with the temperature decrease, reaches a maximum near 60 K, and

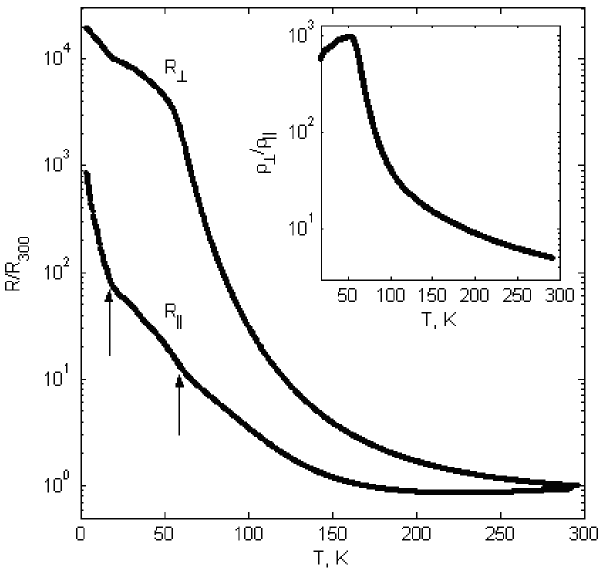

Figure 1. The temperature dependences of the resistance of TiS_3 measured in the longitudinal ($R_{\|}$) and transverse ($R_{\perp}$) directions normalized by the 300 K values. *I*=0.1 μA. Note that below 20 K the resistance is strongly non-linear (Fig. 2,3). The arrows mark the temperatures at which the maxima of the logarithmic derivatives $d\ln R/d(1/T)$ are observed. The *inset* shows the temperature dependence of the ratio $\rho_{\perp}/\rho_{\|}$

then decreases (see inset to Fig. 1).

In addition to the previously known minimum at 250 K, features near 59 and 17 K are seen on the $R_{\|}(T)$ curve (Fig.1) corresponding to the maxima of $d\ln R/d(1/T)$ derivative [5]. In contrast to $R_{\|}$, the transverse resistance $R_{\perp}$ increases monotonically with decrease in *T* below 300 K. However, the features in *R*(*T*) are observed at about the same temperatures in both directions, though the peaks of the derivative of $R_{\perp}(T)$ are wider than those in the longitudinal direction [6].

The current–voltage characteristics along the *b* axis were measured in the temperature range of 4.2–125 K under electric fields up to 200 V/cm. The current–voltage characteristics are almost linear at temperatures above 60 K. *R* begins to depend on *E* near $T \approx 60$ K, where the maximum of the $d\ln R/d(1/T)$ is observed. As *T* decreases, the nonlinearity increases. At high voltages, *V*, $R_d(V)$ tends to saturation (Fig. 2). The nonlinear part of the differential conductivity, $\sigma_{nl} \equiv \sigma_d(V) - \sigma_d(0)$, reaches a maximum at about 50 K. At *T* < 50 K, the temperature dependences of σ_{nl}

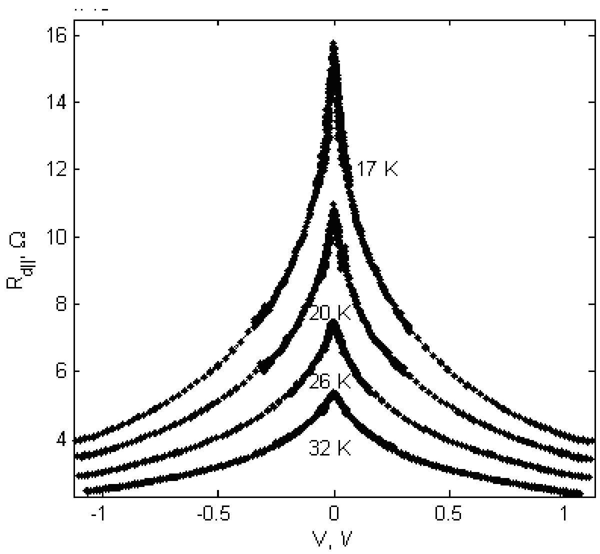

Figure 2. Voltage dependences of the longitudinal differential resistance of the TiS_3 whisker at various temperatures.

reproduce the features of the temperature dependence of the linear conductivity. At the highest voltages σ_{nl} is almost independent of *T*. The results were reported in detail in [5,6]. It should be noted that the $R_d(V)$ curves reported in [5,6] were considerably distorted at |V|<100 mV for *T*<30 K due to high voltage interference. As a result, the zero-voltage peaks seen in Fig. 2 were smeared out, and $R_d(V)$ curves showed threshold behavior.

The fact that resistance becomes voltage dependent at $T \approx 60$ K, which is the temperature of the maximum of the dln*R*/d(1/*T*) derivative, is an evidence of a structural or electronic phase transition in the system. The maxima at $T \approx 60$ K on the temperature dependences of σ_{nl} and $\rho_\perp/\rho_{||}$ confirm that the phase transition occurs. A number of properties of TiS_3 below the transition temperature are similar to those of the quasi-one-dimensional conductors with moving CDW:

1. The maxima of dln*R*/d(1/*T*) derivative for both longitudinal and transverse resistivity at the transition temperature.
2. An increase in the *ab*-plane anisotropy of conductivity with decrease in temperature. The anomaly in the ratio $\rho_\perp/\rho_{||}$ at the transition temperature [7].
3. Strong nonlinearity of the current–voltage characteristics below the transition temperature. The zero-voltage peaks instead of the threshold behavior were reported for $NbSe_3$ nanowires [8].
4. The weak temperature and electric field dependences of nonlinear conductivity in high electric fields.

Thus, the results can be explained by the formation of CDW. However, some properties of TiS_3 are significantly different from those of typical Peierls conductors:

1. The resistivity of TiS_3 at 300 K is $\rho_{300}\approx 2$ Ωcm, i.e. 3-4 orders of magnitude higher than that of the known conductors with CDW.
2. The electron concentration in TiS_3 at room temperature determined from the Hall effect is $n\sim 2\times10^{18}$ cm^{-3} [9]. Up to now, the Peierls transition was observed only in quasi-one-dimensional conductors with a relatively high carrier density ($n\sim 2\times10^{21}$ см$^{-3}$ at $T = 300$ K).
3. The anisotropy of conductivity of TiS_3 in the *ab* plane is comparatively small, $\rho_a/\rho_b\approx 5$ at 300 K (3 times smaller than that for $NbSe_3$ and 30 times smaller than that for TaS_3).

Moreover, recently we have found nonlinear transverse conductivity (along the *a*-axis) at *T*<80 K. The preliminary results are shown in Fig. 3. Therefore, alternative explanations of the effects could be proposed.

In conclusion, indications of a phase transition into collective state at 60 K in the layered semiconductor TiS_3 are found. The transition could be associated with charge ordering, possibly of new type.

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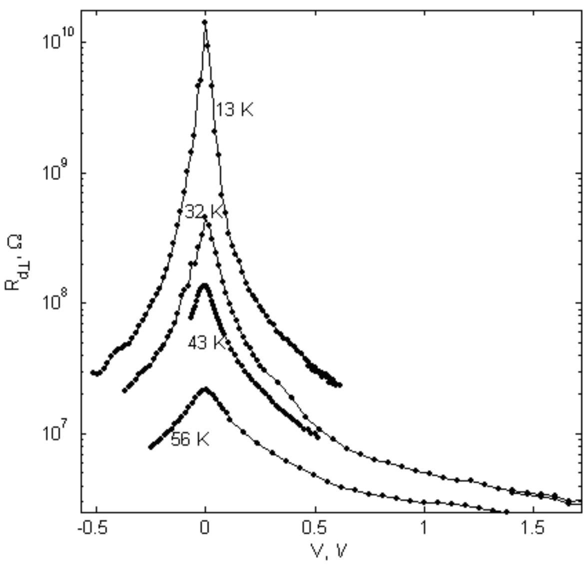

Figure 3. Voltage dependences of the transverse differential resistance of a TiS_3 whisker at various temperatures.

[1] P. Monceau, in Electronic Properties of Inorganic Quasi One-Dimensional Conductors, Vol. 2, Part 2, ed. by P. Monceau (Reidel, Dordrecht, 1985), p. 139.
[2] F. S. Khumalo and H. P. Hughes, Phys. Rev. B: Condens. Matter 22, 2078 (1980).
[3] Pei-Ling Hsieh, C. M. Jackson, and G. Grüner, Solid State Commun. 46, 505 (1983).
[4] S. Kikkawa *et al.*, Phys. Status Solidi A 61, K55 (1980).
[5] I. G. Gorlova and V. Ya. Pokrovskii, JETP Lett. 90, 295 (2009).
[6] I. G. Gorlova *et al.*, JETP 111, 298 (2010).
[7] S. G. Zybtsev *et al.*, Preprint No. 11, IRÉ (Academy of Sciences, Moscow, 1983).
[8] E. Slot *et al.*, Phys. Rev. Lett., 93, 176602 (2004).
[9] O. Gorochov *et al.*, Mater. Res. Bull. 18, 111 (1983).