Effect of defects on phase transitions in tetraselenotetracene chloride, $(TSeT)_2Cl$

P. A. Kononovich, V. N. Laukhin, S. I. Pesotskiĭ, I. F. Shchegolev, and A. G. Khomenko
Institute of Chemical Physics, Academy of Sciences of the USSR

(Submitted 30 November 1982)
Pis'ma Zh. Eksp. Teor. Fiz. **37**, No. 2, 77–79 (20 January 1983)

High-quality single crystals of the organometallic compound $(TSeT)_2Cl$ have been synthesized. The metal-semimetal phase transition in these samples has several new features.

PACS numbers: 72.60. + g, 72.80.Le

In contrast with the case in most known quasi-one-dimensional organometallic compounds, the complex $(TSeT)_2Cl$ undergoes a metal-semimetal, rather than metal-insulator, transition at low temperatures and standard pressure.[1,2] As the temperature is lowered, the conductivity rises, goes through a maximum at 26–27 K, and then falls off, but it does not vanish as $T \to 0$ but instead remains quite high (on the order of the room-temperature conductivity) down to $T = 0.4$ K (Ref. 3). At a pressure ~5 kbar, $(TSeT)_2$ undergoes a first-order phase transition to a new metallic state, which remains stable over the entire temperature range which has been studied, down to 1.3 K (Ref. 4).

The synthesis and crystallization conditions are known to have a strong effect on the properties of quasi-one-dimensional organometallic compounds, since variations in these conditions result in samples with various defect concentrations. For the complex $(TSeT)_2Cl$, good measures of the quality of single crystals are the relative size of the conductivity maximum $(\sigma_{max}/\sigma_{300})$ in the low-pressure phase and the ratio of the room-temperature resistance of the high-pressure metallic phase to its residual resistance (R_{300}/R_{res}). The $(TSeT)_2Cl$ samples synthesized previously[2,5] by various chemical methods have had values of $\sigma_{max}/\sigma_{300}$ ranging from 9 to 15 and ratios R_{300}/R_{res} ranging from 15 to 30.

In the present experiments, $(TSeT)_2Cl$ was synthesized by an electrochemical method[1)] which has previously been used successfully to synthesize extremely high-quality crystals of organic semiconductors from tetramethyltetraselenafulvalene.[6] For the $(TSeT)_2Cl$ crystals synthesized by this method, we find $\sigma_{max}/\sigma_{300} \cong 20$ and $R_{300}/R_{res} \cong 100$. We should also point out that measurements of five crystals of this series yield relative resistances $R(T)/R_{300}$ which agree, within the measurement error, over the entire temperature range studied. For the samples synthesized by the chemical technique, in contrast, even where the values of $\sigma_{max}/\sigma_{300}$ are identical the behavior of the resistance of the low-pressure phase at temperatures below the metal-semimetal transition point is reproducible only qualitatively, and the value of $R_{4.2}/R_{300}$ can vary by a factor of 1.5–2 from crystal to crystal. In summary, the samples synthesized by the electrochemical method are of far higher quality.

The metal-semimetal transition in these new $(TSeT)_2Cl$ samples exhibits several interesting new features. Curve 1 in Fig. 1 is the temperature dependence of the standard-pressure resistance of a single crystal synthesized by the electrochemical method; curve 2 refers to a typical crystal synthesized by a chemical method, with $\sigma_{max}/\sigma_{300} \cong 9$. We see that in the former case the transition occurs at a higher temperature and significantly more rapidly. There is a slight but noticeable hysteresis, which is particularly obvious at the end of the transition. After the transition has been completed, below 15 K, the temperature dependence of the resistance is nonmonotonic: A slight decrease gives way to a new increase below ~6 K.

The low-temperature increase in the resistance observed in these high-quality samples can be suppressed by a magnetic field. The inset in Fig. 1 shows the results obtained with a longitudinal field. We might note in this connection that the longitudinal magnetoresistance is positive and low in the lower-quality crystals, whose resistance is nearly independent of the temperature below 4 K (Refs. 7 and 8). In transverse fields the behavior of the resistance is complicated by the large, positive magnetoresistive effect, which reaches a value ~30% at 4.2 K in a field ~50 kOe and is significantly higher than the corresponding increase in the resistance observed in the crystals synthesized by the chemical method.[7,8] It is important to note, however, that in a field of this magnitude the resistance of the high-quality samples no longer rises below 6 K.

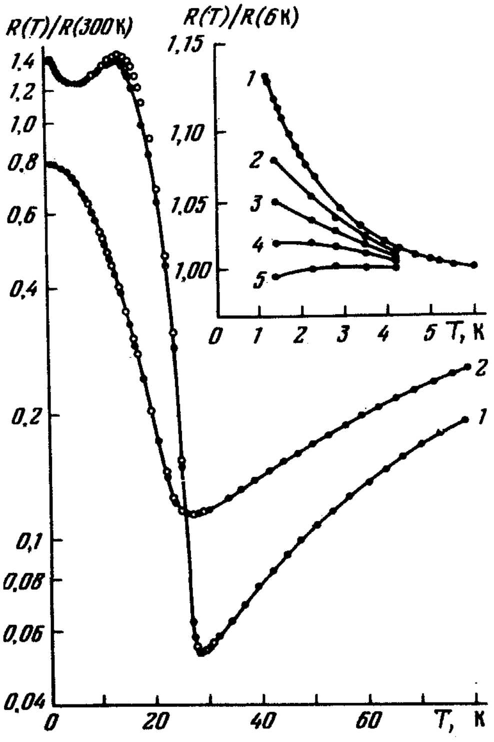

FIG. 1. Typical temperature dependence of $(TSeT)_2Cl$ single crystals at $P = 1$ bar (see the text proper). ● — Cooling; ○—heating. Inset—Effect of a parallel magnetic field on the dependence $R(T)/R$ (6 K) for a crystal synthesized by the electrochemical method. 1—0; 2—20 kOe; 3—30; 4—40; 5—50 kOe.

Figure 2 shows the effect of hydrostatic pressure on the metal-semimetal transition. The most important point to be noted here is that the shift of the beginning of the transition toward lower temperatures is not as pronounced as has previously been believed.[9] As the pressure is raised, the thermal hysteresis becomes more noticeable. This effect and also the suppression of the nonmonotonic behavior of the resistance at low temperatures may be related to the appearance of additional defects in the sample when it is subjected to pressure. We might also note that in the crystals synthesized by the electrochemical method the transition to the high-pressure metallic phase occurs slightly earlier: at $P \cong 4$ kbar instead of the 5 kbar characteristic of the lower-quality crystals.[4]

A nonmonotonic behavior of the resistance has not been observed previously in organometallic compounds at low temperatures. The nature of this effect is not clear at this point and requires further study. If the decrease in the resistance below 15 K can be attributed to ordinary phonon freezing, under the assumption that the metal-semimetal transition is completely over at this temperature, then the subsequent increase in the resistance might be caused, for example, by quantum interference ef-

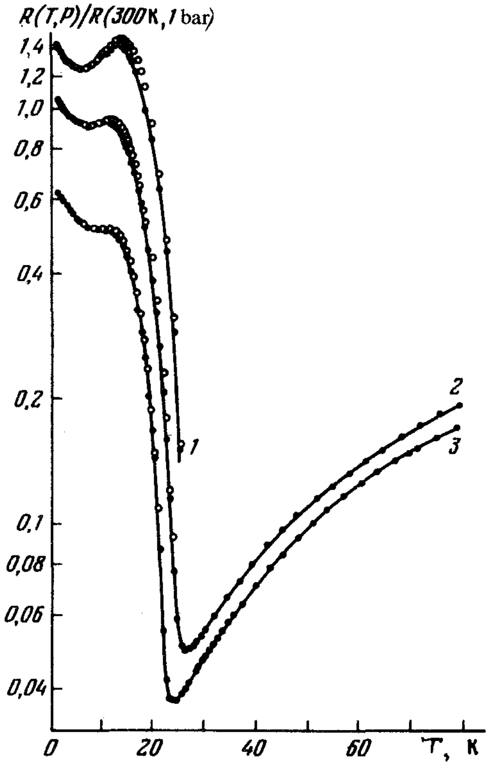

FIG. 2. Temperature dependence of the resistance of $(TSeT)_2Cl$ single crystals synthesized by the electrochemical method at the following pressures: 1—1; 2—2.5; 3—3.5 kbar. ●—Cooling; ○—heating.

fects.[10] Evidence for this interpretation comes from the fact that this increase disappears in strong magnetic fields.

I wish to thank D. E. Khmel'nitskiĭ for useful discussions and É. B. Yagubskiĭ for interest in this study.

[1)] The synthesis conditions will be published separately in Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya (Bulletin of the Academy of Sciences of the USSR, Division of Chemical Sciences).

---

[1] I. F. Shchegolev and E. B. Yagubckii, in Extended Linear Chain Compounds (ed. J. S. Miller), Plenum, New York, Vol. 2, 1982, p. 385.
[2] O. N. Eremenko, S. P. Zolotukhin, A. I. Kotov, M. L. Khidekel', and É. B. Yagubskiĭ, Izv. Akad. Nauk. SSSR, Ser. Khim. 1507 (1979).
[3] V. B. Ginodman, L. N. Zherikhina, and E. E. Yurchakevich, Pis'ma Zh. Eksp. Teor. Fiz. **30**, 290 (1979) [JETP Lett. **30**, 268 (1979)].
[4] V. N. Laukhin, A. I. Kotov, M. L. Khidekel', I. F. Shchegolev, and É. B. Yagubskiĭ, Pis'ma Zh. Eksp. Teor. Fiz. **28**, 284 (1978) [JETP Lett. **28**, 260 (1978)].
[5] A. V. Zvarykina, V. N. Laukhin, E. E. Yurchakevich, and É. B. Yagubskiĭ, Zh. Eksp. Teor. Fiz. **83**, 799 (1982) [Sov. Phys. JETP **56**, 448 (1982)].
[6] K. Bechgaard, C. S. Jacobsen, K. Mortensen, H. J. Pedersen, and N. Thorup, Solid State Commun. **33**, 1119 (1980).

[7] S. P. Zolotukhin, Yu. S. Karimov, and I. F. Shcheglov, Zh. Eksp. Teor. Fiz. **76**, 377 (1979) [Sov. Phys. JETP **49**, 192 (1979)].

[8] V. N. Laukhin and D. N. Fedutin, Zh. Eksp. Teor. Fiz. **83**, 1212 (1982) [Sov. Phys. JETP (to be published)].

[9] V. N. Laukhin and I. F. Shchegolev, Zh. Eksp. Teor. Fiz. **78**, 2332 (1980) [Sov. Phys. JETP **51**, 1170 (1980)].

[10] A. I. Larkin and D. E. Khmel'nitskiĭ, Usp. Fiz. Nauk **136**, 536 (1982) [Sov. Phys. Usp. **25**, 185 (1982)].

Translated by Dave Parsons
Edited by S. J. Amoretty