

146. Electrical Properties and Structure of the Organic Metallic Compound bis (Tetraselenotetracene)-Iodide, (TSeT)₂-I

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Summary

The preparation of the new organic metallic compound (TSeT)₂-I is reported. The crystal structure of the free donor, TSeT, is discussed and compared with the crystal structure of (TSeT)₂-I. The latter has the orthorhombic space group $P_{2_1}2_12$ and hence is not isomorphous with the analogous compounds (TSeT)₂-Cl and (TSeT)₂-Br, described by *Shchegolev et al.* [4].

In contrast to those complexes (TSeT)₂-I consists of only one set of crystallographically equivalent chains and therefore its transition to the low-temperature conducting state (*Fig. 6*) is also of different type.

The d.c. resistivity at 300 K ranges from 10^{-3} to $1.5 \cdot 10^{-4} \Omega \text{ cm}$. The temperature dependence of the d.c. resistivity of the title compound is given: in the temperature range from 300 to 80 K the normalized d.c. resistivity is described by $\rho(T)/\rho(300) \propto T^{1.7}$. Between 80 and 70 K a slight deviation from the above law has been detected which is taken as an indication of a phase transition; its nature is, however, not yet definable. The low-temperature conducting state reached at about 70 K shows an almost constant resistivity in the interval 60 K to 45 K. Its normalized d.c. resistivity in the range 4.5 K-50 K is described by $\rho(T)/\rho(300) \propto (T-T_m)^3$, with $T_m=50 \text{ K}$. The value of the normalized resistivity extrapolated to 0 K is 0.75.

Introduction. - We wish to report upon a new organic metallic compound of the quasi-1-dimensional metallic class, viz. bis(tetraselenotetracene)-iodide, (TSeT)₂-I.

We have studied the orthorhombic structure of this complex in continuation of our work [1-3] on the chalcogenated metallic compounds bis(tetrathiotetracene)-triiodide, (TTT)₂-I₃, and tri(tetraselenotetracene)-*o*-chloranil, (TSeT)₃-*o*-chloranil (*Fig. 1*).

Recently *Shchegolev et al.* [4] have reported on the compound (TSeT)₂-Cl, prepared by cooling a solution of TSeT and the oxidants FeCl₃ or N(CH₃)₄[FeCl₄] in dimethylformamide. The crystal structure together with the temperature dependence of the electrical conductivity and the paramagnetic susceptibility of

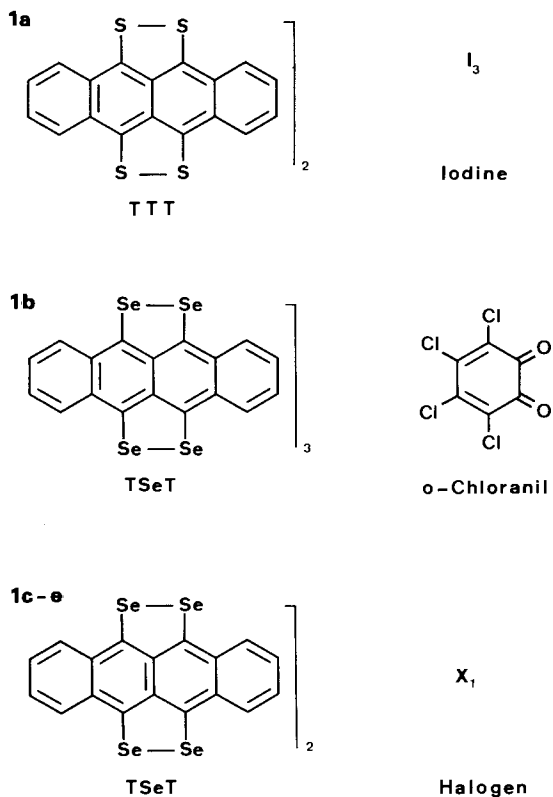


Fig. 1. Formulas of organic metallic compounds

1a
 $(\text{TTT})_2\text{I}_3$: Complex formed upon oxidation of 5,6,11,12-tetrathiotetracene with iodine ([2] [3] and ref. therein).

1b
 $(\text{TSeT})_3(\text{o-chloranil})$: Complex formed upon oxidation of 5,6,11,12-tetraselenotetracene with *o*-chloranil [1].

1c
 $(\text{TSeT})_2\text{X}_1$; X = Cl; complex formed upon oxidation of 5,6,11,12-tetraselenotetracene with FeCl_3 or $[\text{N}(\text{CH}_3)_4]\text{FeCl}_4$ as reported by *Shchegolev et al.* [4].

1d
 $(\text{TSeT})_2\text{X}_1$; X = Br; complex mentioned by *Shchegolev et al.* [4].

1e
 $(\text{TSeT})_2\text{X}_1$; X = I; complex formed upon oxidation of 5,6,11,12-tetraselenotetracene with iodine (this paper).

single crystals were reported. The $(\text{TSeT})_2\text{-Br}$ complex was mentioned to be isostructural to $(\text{TSeT})_2\text{-Cl}$ and having similar physical properties, but no reference was made to $(\text{TSeT})_2\text{-I}$ reported here, nor to its possible preparation.

Experimental Part. - The preparation of the 5,6,11,12-tetraselenotetracene (TSeT) was performed according to the procedure of *Marschalk* [5] by reaction of 5,11-dichloro-tetracene with selenium (*Alfa Inorganics*; 99.9%) in boiling Dowtherm (an eutetic of biphenyl and diphenyloxyde, b.p. $\sim 260^\circ$) under a nitrogen atmosphere.

The simplified method claimed by *Perez-Albuerne* [6] according to which unsubstituted tetracene is directly converted into the tetraselenoderivative by selenium (in analogy to the reaction of tetracene with sulfur) appeared to us as being inoperable. Prepurification of the raw material was performed by oxidizing its suspension in formic acid with air, and reducing the blue solution of the cation radical (TSeT^+) with TiCl_3 .

This step eliminated most of the unreacted selenium present. Prior to the crystal growth, TSeT was extensively purified by up to 16 runs in a gradient sublimator at about 10^{-5} Torr. Crystals of TSeT were grown by subliming TSeT at 320° in a purified Argon flow (15 l/h) passing through a silica tube of approx. 2 cm in diameter. The crystals grew as long needles and were of orthorhombic structure (see below).

The $(\text{TSeT})_2\text{-I}$ complex was grown by the cosublimation procedure described previously [2] [3]. Two types (a and b) of single crystals in the form of needles in dimensions of up to $1.5 \text{ cm} \times 20 \mu \times 200 \mu$ were obtained. Type a crystals have metallic properties and show a silvery lustre. Type b crystals, the structure of which is still under investigation, show a golden lustre and

exhibit a semiconducting temperature dependence of the electrical conductivity. Experiments to grow the different phases separately are in progress.

The d.c. conductivity measurements were performed by standard 4-probe techniques as described in [7]. First, the temperature dependence of the d.c. conductivity of dozens of crystals were measured down to the temperature of liquid nitrogen. Those exhibiting the strongest metallic temperature dependence were selected and measured down to the temperature of liquid helium.

The crystal lattice constants were refined by least square analysis of the setting angles of twelve reflexions centered through narrow slits of a *Picker* automatic 4-circle diffractometer FACS-I, *MoK α* radiation (graphite monochromator).

Results and discussion. - Crystal data for TSeT (Space group $P_{2_12_12_1}$), and the complex (TSeT)₂-I (Space group $P_{2_12_12}$) are given in *Table 1*. Both structures are exceptions to the general rule that centrosymmetric molecules crystallize in centrosymmetric space groups. As a comparison, *Shchegolev et al.* [4] found for (TSeT)₂-Cl and (TSeT)₂-Br the monoclinic space group $P_{2/n}$ with $a=b=17.444$ Å and $c=5.118$ Å.

A projection on the (*a,b*)-plane of the crystal structure of the free donor, TSeT, is given in *Figure 2*. The molecules are planar within experimental error. Interplanar spacings within a stack are 3.42 Å. The intermolecular distances between selenium atoms of molecules in neighbouring stacks are also given in *Figure 2*.

The crystal structure viewed down the *c*-axis of (TSeT)₂-I is given in *Figure 3*. As in other good one-dimensional organic conductors, the structure is dominated by stacks of donor molecules along the direction of high electrical conductivity. The interplanar stacking distance is 3.40 Å. All TSeT-molecules are crystallographically equivalent in contrast to the TSeT-molecules in the structures of (TSeT)₂-Cl and (TSeT)₂-Br [4]. The I[⊖] anions lie on the twofold axes parallel to *c*. The distances between I[⊖] and the 8 selenium atoms of its surrounding

Table I. *Crystal data*^{a)}

	TSeT	(TSeT) ₂ -I
Space group	$P_{2_12_12_1}$	$P_{2_12_12}$
<i>a</i> (Å)	17.184	18.366
<i>b</i> (Å)	15.719	17.450
<i>c</i> (Å)	5.598	5.077
<i>v</i> (Å ³)	1512	1627
<i>z</i>	4	2
Final R-factor	0.134 (837 reflections)	0.085 (1404 reflexions)
Angle between long molecular axis and <i>c</i> (°)	38	42
Angle between medium molecular axis and <i>c</i> (°)	83	88

^{a)} Tables of atomic coordinates and structure factors are available from *G.R.* on request.

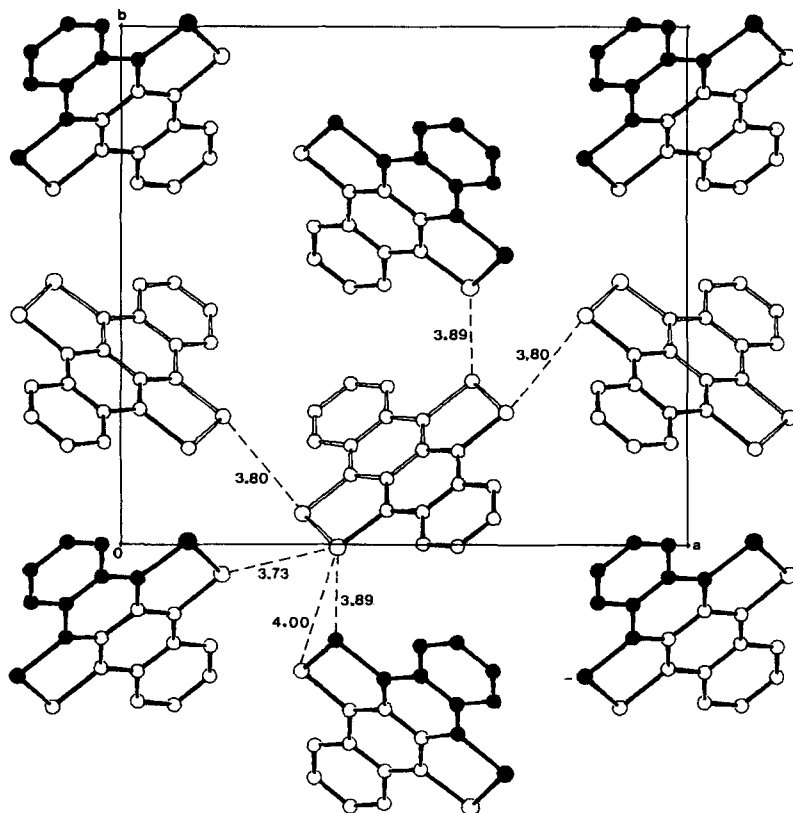


Fig. 2. Free donor TSeT: Projection of the orthorhombic structure on the (a,b)-plane. (Increased shading of the molecules (no shade - shaded bonds only - shaded bonds and atoms) indicates increased Z/c values).

stacks are also given in *Figure 3*. The numbers given in the middle of the TSeT molecules and in parentheses represent Z/c coordinates.

The TSeT molecules of the $(\text{TSeT})_2\text{-I}$ complex are not exactly planar. The two selenium atoms nearest (3.42 Å) to the I^\ominus -ions lie significantly (0.25 Å) out of the least squares plane calculated with the non-hydrogen atoms of a TSeT molecule. The symmetry of the complexed TSeT molecules is thus C_s .

The molecular overlaps of the TSeT molecules in the free donor and in the complex, $(\text{TSeT})_2\text{-I}$ are illustrated in *Figures 4a* and *b*. In the non-complexed TSeT (*Fig. 4a*) the distance between the two nearest selenium atoms of two neighbouring molecules within a stacks is 4.07 Å. In $(\text{TSeT})_2\text{-I}$ this distance is shortened to 3.45 Å.

In order to evaluate the range of the resistivity of single crystals at room temperature, crystals were selected under the microscope and mounted on glass slides. The two contacts for simple resistance measurements were made of Pt paste 308, *Degussa*. The resistivity values thus obtained range from 10^{-3} to 1.5

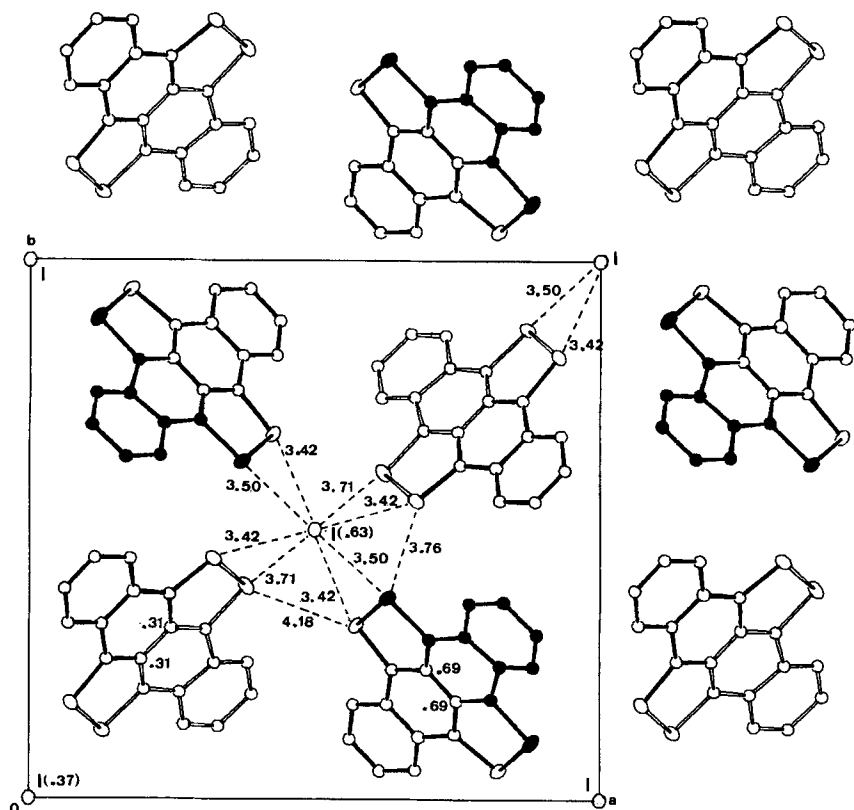


Fig. 3. $(TSeT)_2-I$: Projection of the structure on the (a,b)-plane. (Increased shading of the molecules (no shade - shaded bonds only - shaded bonds and atoms) indicates increased Z/c values).

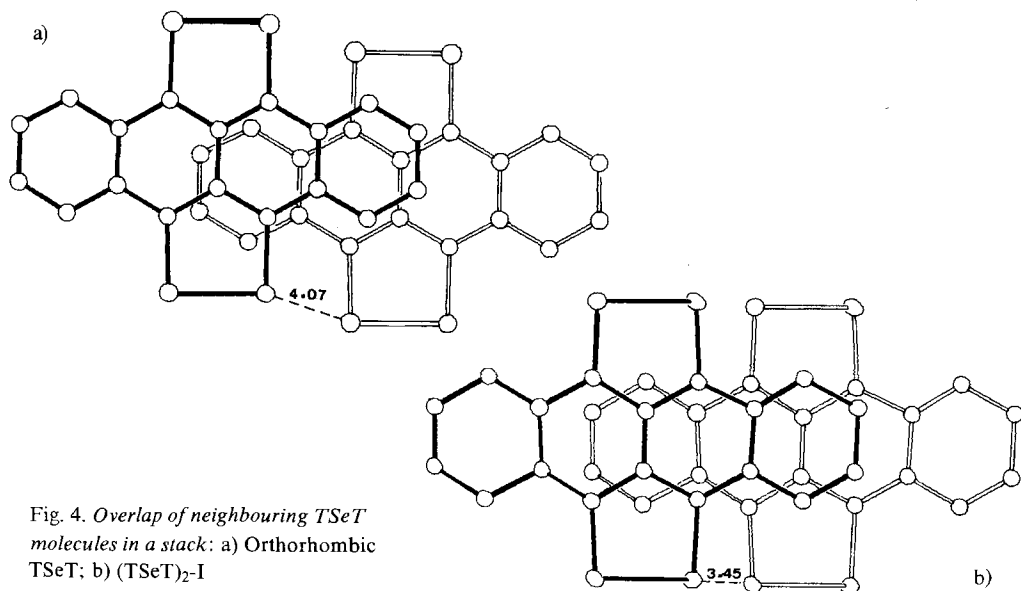


Fig. 4. Overlap of neighbouring $TSeT$ molecules in a stack: a) Orthorhombic $TSeT$; b) $(TSeT)_2-I$

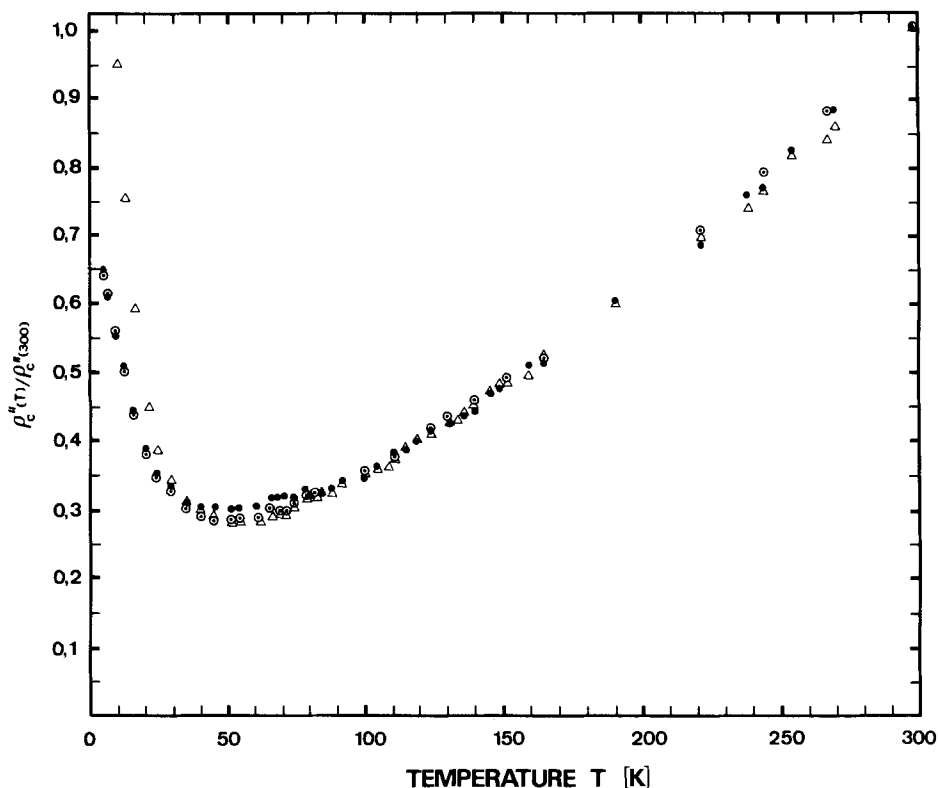


Fig. 5. Normalized d.c. resistivity of $(TSeT)_2-I$ single crystals

△ dimensions: $1\text{ cm} \times 72\ \mu \times 47\ \mu$; resistivity at 300 K: $9.4 \cdot 10^{-4}\ \Omega\text{ cm}$

● dimensions: $1\text{ cm} \times 48\ \mu \times 43\ \mu$; resistivity at 300 K: $5.7 \cdot 10^{-4}\ \Omega\text{ cm}$

○ dimensions: $1\text{ cm} \times 48\ \mu \times 35\ \mu$; resistivity at 300 K: $8.3 \cdot 10^{-4}\ \Omega\text{ cm}$

$10^{-4}\ \Omega\text{ cm}$. This relatively wide spread may be due to irregularities in the growth pattern of the crystals (strong tendency to form bundles of fibres). Work to improve the sample quality is underway.

Figure 5 shows the temperature dependence of the d.c. resistivity of 3 single crystals of $(TSeT)_2-I$ normalized to its value at 300 K. The most striking feature is the fact that the behaviour in the region of 4.2 K to 50 K suggests a finite value (0.75) of the normalized resistivity at $T=0\text{ K}$. The minimum in the resistivity plot is rather broad and is practically flat over the range 45 K to 60 K. Between 60 K and 80 K a slight deviation from the otherwise very steady metallic behaviour in the temperature interval above the minimum is just detectable. In the temperature region 80 K to 300 K the data fit the expression

$$\rho(T)/\rho(300) \propto T^{1.7}. \quad (1)$$

For some other crystals an exponent of 1.6 is more appropriate.

The steep rise of crystal 1 (Fig. 5) on the low temperature side of the

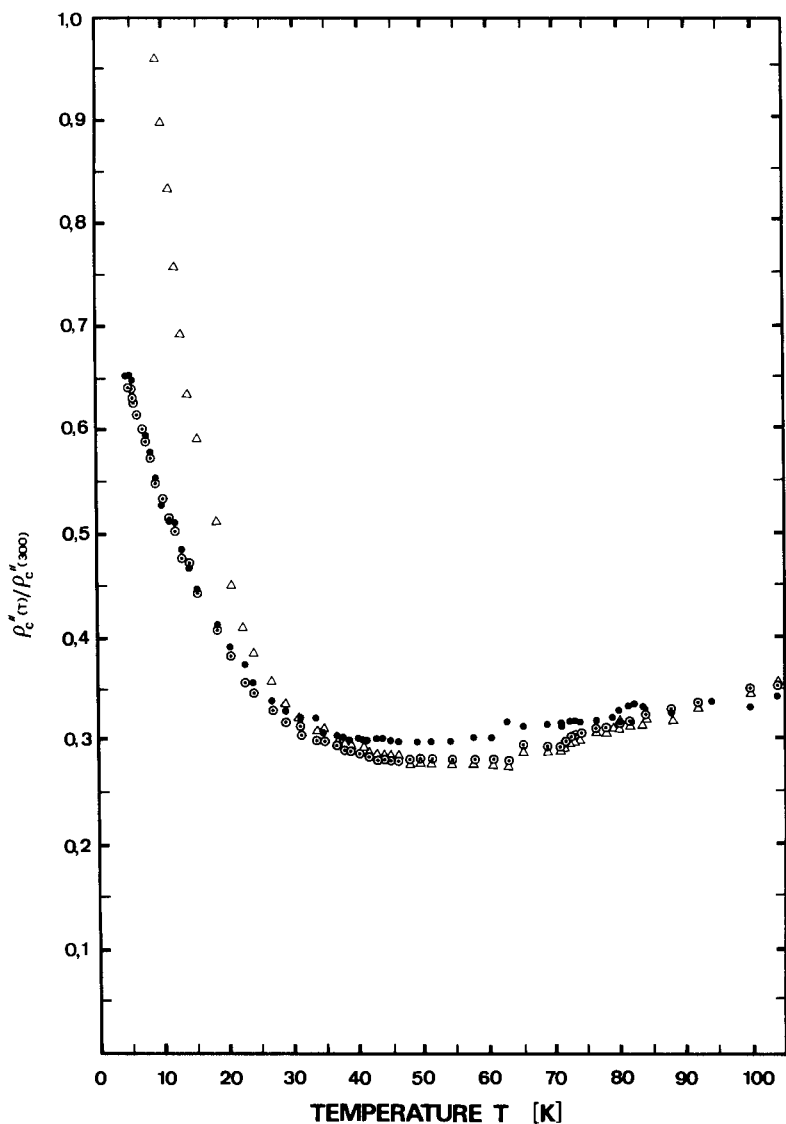


Fig. 6. Details of the low temperature normalized d.c. resistivity (same crystals as in Fig. 5)

resistivity curve is typical for a physical crystal defect. Crystals 2 and 4 (Fig. 6) however, are representative for the intrinsic behaviour of our best samples so far and can be fitted in the temperature interval from 4.2 K to 50 K within the experimental accuracy of 3% by

$$\rho(T)/\rho(300) = a(T - T_m)^3 + b \quad (2)$$

with $a = 3.75 \times 10^{-6} \text{ K}^{-3}$, $b = 0.285$, $T_m = 50 \text{ K}$.

We have some evidence that some lower value for the extrapolated value of $\rho(0)/\rho(300)$ might be possible in future.

Shchegolev et al. [4] suggest for their $(\text{TSeT})_2\text{-Cl}$ system a *Peierls* transition in one of the two inequivalent sets of conducting TSeT chains, whilst the other set would persist in a metallic state as inferred from the paramagnetic data. These authors argue that the increase in resistivity in this temperature region could still be characteristic of a metallic electron gas on one set of the chains; the scattering mechanism, however, would be due to a phonon system the spectrum of which is substantially changed at the transition.

In contrast to the $(\text{TSeT})_2\text{-Cl}$ and $(\text{TSeT})_2\text{-Br}$ systems, all the chains of TSeT in the $(\text{TSeT})_2\text{-I}$ crystals are equivalent. There must therefore be a difference in the nature of the transition of the high temperature metallic state to the low temperature *Peierls* state. In $(\text{TSeT})_2\text{-I}$ every chain of TSeT has the same probability to undergo a *Peierls* transition. The transition, however, will not take place on all the chains simultaneously. Thus, disorder between the chains will occur in addition to disorder within the chains. Therefore, a finite occupied density of states within the *Peierls* gap will prevent the system from behaving as a pure semiconductor below the transition temperature. In order to clarify these points, further electrical as well as magnetic and calorimetric measurements are underway.

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