Stabilization under pressure of the metallic state in electrically conducting organic tetraselenotetracene salts $(TSeT)_2Br_xCl_{1-x}$

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Under an applied hydrostatic pressure, tetraselenotetracene complexes of composition $(TSeT)_2Br_xCl_{1-x}$ $(0\leqslant x\leqslant 1)$ undergo a first-order phase transition to a new metallic state which is stable on cooling over the whole temperature range down to 1.3 K. The pressure at which this transition takes place decreases linearly with increasing x from 5 kbar for $(TSeT)_2Cl$ to 2.2 kbar for $(TSeT)_2Br$. The resistance of the high-pressure phase of the complexes studied falls practically linearly with decreasing temperature and below 10 K becomes the residual resistance characteristic of each composition.

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I. INTRODUCTION

There have been earlier reports[1–3] of the synthesis and structure and of the main properties of the new organic quasi-one-dimensional metals, tetraselenotetracene chloride and bromide with compositions $(TSeT)_2Cl$ and $(TSeT)_2Br$. Their conductivity goes through a maximum as the temperature is lowered but does not vanish as occurs for the great majority of organic quasi-one-dimensional metals known at present; it remains fairly large (of the order of the room temperature value) down to extremely low temperatures.[1,4]

Crystals of $(TSeT)_2Cl$ and $(TSeT)_2Br$ are isomorphous and comprise regular stacks of positively charged planes of tetraselenotetracene molecules; the Cl or Br anions are situated between the stacks.[2] The specific conductivities of these compounds are of similar magnitude at room temperature and have fairly high values equal to $(1\text{–}2)\times 10^3\,\Omega^{-1}\cdot\text{cm}^{-1}$. On reducing the temperature, $(TSeT)_2Cl$ and $(TSeT)_2Br$ undergo a metal-semimetal phase transition at $T\approx 19$ K and $T\approx 26$ K respectively.[5,6] Under a hydrostatic pressure $P\approx 5$ kbar a first-order phase transition takes place in $(TSeT)_2Cl$ to a new metallic state which remains stable down to 1.3 K and its residual resistivity at $T\lesssim 10$ K is $1.1\times 10^{-5}\,\Omega\cdot\text{cm}$.[7,8] It could be expected that hydrostatic pressure would have a similar effect on $(TSeT)_2Br$, which is a structural analog of the chloride. In addition, it would be extremely interesting to obtain compounds of a solid solution type of these isomorphic complexes with composition $(TSeT)_2Br_xCl_{1-x}$ and to study the influence of hydrostatic pressure on their conducting properties. The present work is devoted to elucidating these problems.

SPECIMENS AND METHOD OF MEASURING

In the present work, $(TSeT)_2Cl$ complexes were studied which had been synthesized immediately before the measurements[1)] by a method which differed from that described earlier.[1,3] The main difference was that $HgCl_2$ was used to oxidize TSeT and not $CuCl_2$. The $(TSeT)_2Br$ complex was synthesized as before[3] by oxidizing TSeT with anhydrous $CuBr_2$. Complexes of the composition $(TSeT)_2Br_xCl_{1-x}$ with $x = 0.1$, 0.5 and 0.9 were obtained by oxidizing TSeT with a mixture of $CuBr_2$ and $CuCl_2$ of the appropriate molar proportions. The final composition of the compounds was determined by an elemental analysis for C, H, Cl and Br. The accuracy in determining the Cl and Br content was ± 0.3 wt.% (using x-ray fluorescence analysis).

The crystals obtained were in the form of black needles with transverse dimensions 15 to 20 μm and length up to 2 mm. The conductivity was measured at constant current by the four-lead method in the high-conductivity c-axis direction. For this purpose the crystals were stuck with graphite paste to the ends of 20 μm diameter platinum wires. Pressure was applied in a piston and cylinder type chamber and was fixed at room temperature. The pressure fell by about 25 to 30% on cooling to 4.2 K. The pressure-transmitting medium was a silicon-organic liquid GKZh-94. The design of the stop of the high-pressure chamber was such that two specimens could be stuck on simultaneously in immediate proximity to one another. In this way the relative error in determining the magnitudes of the phase transition pressure for complexes of different composition could be reduced. It was not more than ± 0.1 kbar. Calibration of the high pressure cell was carried out according to the phase transition in $(TSeT)_2Cl$.[8] Measurements were made on several single crystals of each composition. We did not observe appreciable differences between the properties of different specimens from the same synthesis.

EXPERIMENTAL RESULTS

The temperature dependence of the relative change in conductivity at atmospheric pressure is shown in Fig. 1 for complexes of different composition. It can be seen that the conductivity of the complex $(TSeT)_2Cl$ obtained by the method described above reaches a maximum at 26 K as found before,[1] but our maximum is appreciably higher and steeper: $\sigma_{\max}/\sigma_{300} = 14$ to 15. On lowering the temperature further, a sharp transition to the semi-metallic state is observed: $\sigma_{4.2}/\sigma_{300}$ is then ≈ 0.7. A similar temperature dependence is observed for $(TSeT)_2Br$, but here the conductivity reaches a maximum at $T_{\max}\approx 35$ K and the ratio $\sigma_{\max}/\sigma_{300} = 7$ to 8, while $\sigma_{4.2}/\sigma_{300}\approx 0.1$.

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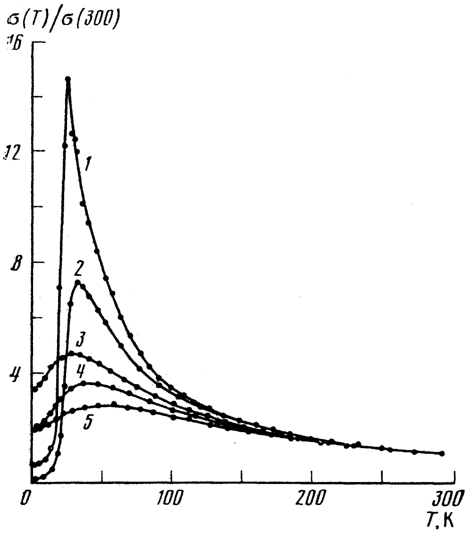

FIG. 1. Temperature dependence of the relative change in c-axis conductivity of the complexes: 1—$(TSeT)_2Cl$, 2—$(TSeT)_2Br$, 3—$(TSeT)_2Br_{0.1}Cl_{0.9}$, 4—$(TSeT)_2Br_{0.9}Cl_{0.1}$, 5—$(TSeT)_2Br_{0.5}Cl_{0.5}$.

We should point out that the maximum in the conductivity obtained for $(TSeT)_2Cl$ seems close to the limiting possible value for the compound. In fact, since the resistivity of the complexes studied falls almost linearly with temperature ($\rho \sim T^{1.06}$),[1] then for an ideally pure crystal of $(TSeT)_2Cl$ for which $T_{\max} \approx 26$ K, the ratio $\sigma_{\max}/\sigma_{300}$ should be approximately $\rho_{300}/\rho_{26} \approx 300/26 \approx 12$. The observed 14-fold increase in conductivity is to be explained by the fact that in the present case the resistivity decreases a little faster than linearly and $\rho \sim T^{1.15}$.

A similar calculation for $(TSeT)_2Br$, for which $T_{\max} \approx 35$ K, gives $\sigma_{\max}/\sigma_{300} = \rho_{300}/\rho_{35} \approx 300/35 \approx 9$ which is slightly greater than the value obtained experimentally. This is evidently due to the $(TSeT)_2Br$ specimens being "dirtier" than $(TSeT)_2Cl$ and the contribution to the resistivity due to scattering by impurities and defects already becomes appreciable for $T > 35$ K. As a result, the conductivity maximum is lowered and broadened.

When bromine is partially substituted for chlorine, whose ionic radius is smaller than that of bromine, complexes of composition $(TSeT)_2Br_xCl_{1-x}$ are formed which are, apparently, organic metals of the disordered solid solution type. As for ordinary metals,[9] the disorder increases as $x \to 0.5$. As evidence of this, the maximum conductivity of $(TSeT)_2Br_xCl_{1-x}$ complexes decreases in magnitude as $x \to 0.5$ and shifts to higher temperatures while the low-temperature metal–semimetal transition is smeared out; at the same time the resistivity at helium temperatures increases (Fig. 1).

When pressure is applied at room temperature, the resistivity of all the complexes studied initially decreases smoothly (Fig. 2). On reaching 5 kbar a discontinuous decrease in the resistivity of $(TSeT)_2Cl$ specimens to about half its value is observed as in earlier measurements.[7,8] On increasing the pressure further, the resistivity continues to decrease but noticeably more slowly then before the jump. Such a discontinuity is also observed for $(TSeT)_2Br$, but at 2.2 kbar, and for compounds $(TSeT)_2Br_xCl_{1-x}$ at $P = 2.5$, 3.0 and 4.4 kbar respectively for $x = 0.9$, 0.5 and 0.1 (Fig. 2).

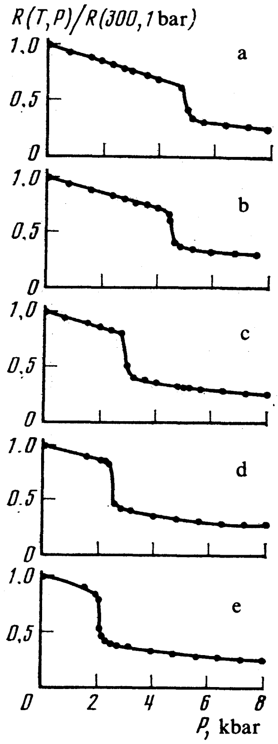

FIG. 2. Relative change in resistivity of the complexes on application of pressure at room temperature: a—$(TSeT)_2Cl$, b—$(TSeT)_2Br_{0.1}Cl_{0.9}$, c—$(TSeT)_2Br_{0.5}Cl_{0.5}$, d—$(TSeT)_2Br_{0.9}Cl_{0.1}$, e—$(TSeT)_2Br$.

This behavior of the resistivity indicates that a phase transition to a new metallic phase takes place under pressure in the compounds. This transition is of the same nature as in $(TSeT)_2Cl$ studied earlier,[7,8] and the temperature dependence of the resistivity of the high-pressure phase also confirms this (Fig. 3). In what follows we shall call it phase II and the low-pressure phase, phase I. It can be seen from Fig. 3 that the phase-II resistivity for all complexes falls practi-

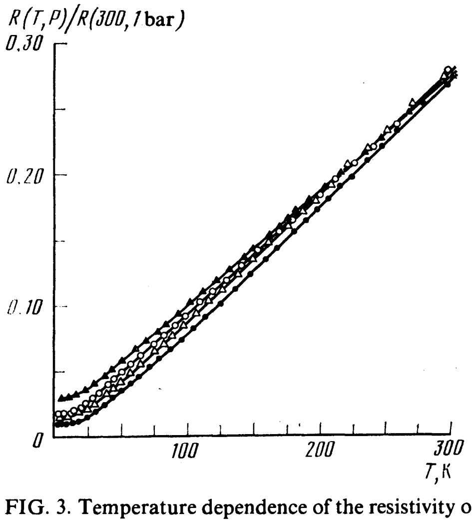

FIG. 3. Temperature dependence of the resistivity of the high-pressure phase of the complexes: ●—$(TSeT)_2Cl$, ○—$(TSeT)_2Br_{0.5}Cl_{0.5}$, ▲—$(TSeT)_2Br_{0.9}Cl_{0.1}$, △—$(TSeT)_2Br$—at $P =$ 8 kbar, fixed at room temperature.

cally linearly with decreasing temperature and below ~ 10 K goes to the residual value, characteristic for each composition. We note that the resistivity in fact decreases a little faster than is shown in the figure, since the pressure in the chamber decreases on cooling and the resistivity then increases.

DISCUSSION

The magnitude of the residual resistivity of the present specimens, as in ordinary metals, presumably depends on the number of impurities and defects in the crystal lattice. The results given show that purer and more perfect $(TSeT)_2Cl$ specimens were obtained in the present work than previously[7] since they have under pressure $\rho_{300}/\rho_{res} \approx 27$ to 28, while before[7] $\rho_{300}/\rho_{res} \approx 14$ to 15 under the same pressure. This also explains our higher maximum conductivity at atmospheric pressure than previously.[1]

We found that for phase II of $(TSeT)_2Br$ $\rho_{res} \approx (0.7$ to $0.8) \times 10^{-5} \Omega\cdot cm$ and $\rho_{300}/\rho_{res} \approx 16$ to 17. It is surprising that we obtained $\rho_{300}/\rho_{res} \approx 15$ to16 for phase II of the complex $(TSeT)_2Br_xCl_{1-x}$ with $x = 0.5$, as this is close to the ratio for the pure bromide, while at atmospheric pressure these specimens appeared dirtier—the conductivity maximum was broader and apparently lower than for $(TSeT)_2Br$ (Fig. 1). On the other hand, the ratio $\rho_{300}/\rho_{res} \approx 9$ for phase II of the complex with $x = 0.9$ which has the maximum slightly higher than for $x = 0.5$. Complexes with $x = 0.1$ behave qualitatively in the same manner. This seems to indicate that, in the course of the crystallographic rearrangement of the lattice during the phase transition under pressure, some reordering takes place which is apparently a maximum for $x = 0.5$.

As we noted in the Introduction, $(TSeT)_2Cl$ and $(TSeT)_2Br$ are isomorphic. In addition, the difference in ionic radius for chlorine and bromine is only 8.3%. Consequently unlimited solubility of one in the other is possible as in ordinary metals, with the formation of a continuous range of solid solutions with composition $(TSeT)_2Br_xCl_{1-x}$. It might be expected that the properties of these complexes should change almost linearly with composition. In fact, it can be seen from Fig. 4 that the pressure at which the phase transition occurs in the complexes studied decreases monotonically with increasing x on going from $x = 0$ to $x = 1$, i.e., with increasing the molecular weight of the compound. We can then suppose that for organic metals, as for pure elements, an empirical homologous rule holds: the action of high pressure usually leads to the same changes in a number of properties, in particular the structure, as an increase in atomic number (atomic weight) for elements of one group of the periodic table.[10]

In this connection it would be interesting to consider the homologous series of compounds $(TSeT)_2X$, where X is F, Cl, Br and I. By extrapolating the composition (molecular weight) dependence of the phase transition pressure in both directions we find that the $(TSeT)_2F$ complex which has a lower molecular weight than $(TSeT)_2Cl$, should be isomorphous with TSeT chloride and bromide at atmospheric pressure and undergo a transition to phase II in the region of 6 kbar at room temperature (Fig. 4). The analogous compound $(TSeT)_2I$ with higher molecular weight than $(TSeT)_2Br$ should have the properties and structure of phase II.

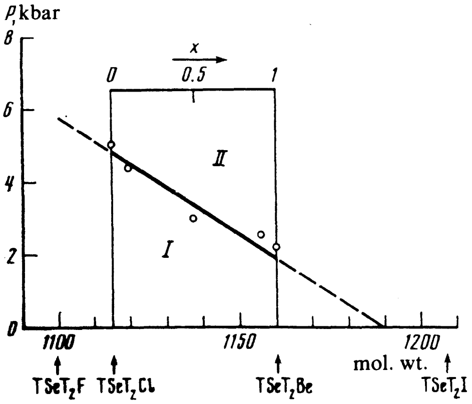

FIG. 4. Dependence of the phase-transition pressure at room temperature on the composition (molecular weight) of the complexes. The solid line separates the region of existence of the low-pressure phase (I) from the high-pressure phase (II) for the complexes $(TSeT)_2Br_xCl_{1-x}$ $(0 \leqslant x \leqslant 1)$.

Unfortunately, the $(TSeT)_2F$ complex has not been obtained so far. On oxidizing TSeT with iodine in organic solutions, the composition $(TSeT)_2I$ is not obtained. It can only be obtained in gaseous reactions.[12] It then turns out, in fact, not to be isomorphous with the chloride and bromide. The iodide obtained in this way has the lower orthorhombic symmetry with the space group $P2_12_12_1$ (Ref. 12) while the chloride and bromide are tetragonal with space group $P4_{2/n}$ (Ref. 2). This provides a basis for thinking that phase II should also have a structure of lower symmetry than phase I. This conclusion can also be reached from the following considerations: $dT/dP > 0$ for the $(TSeT)_2Cl$ phase transition under pressure near room temperature,[8] while the higher-temperature phase (in this case phase I) is always of higher symmetry, as it should be, than the low-temperature phase II at the same pressure.

We note, however that the $(TSeT)_2I$ obtained[12] does not remain a metal, nevertheless, over the whole temperature range, but with decreasing temperature goes over into the semimetallic state as does phase I. It is possible that the low-temperature metal–semimetal transition associated with this class of compounds is determined not only by the type of crystal structure but also by the characteristic parameters of the unit cell, by the amount of impurity, and by a number of reasons which are so far not completely understood.[2)] We can also imagine that the diagram shown (Fig. 4) is of more complicated form and that there is another phase transition line as yet unknown to us. It would be extremely interesting to study the $(TSeT)_2I$ complex under pressure. It is not impossible that for this compound a phase transition to the metallic state takes place at a pressure appreciably less than 2 kbar (the transition pressure for $(TSeT)_2Br$) and that this is stable over the whole temperature range, as is phase II.

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1) We may note that on long exposure to the atmosphere, $(TSeT)_2Cl$ specimens evidently oxidize. As a result, the number of impurities and defects grows, leading to a lowering of the maximum conductivity at atmospheric pressure and to an increase in the residual resistivity of the high-pressure phase. For example, six months after synthesis our $(TSeT)_2Cl$ specimens had a maximum conductivity which was not 14 or 15 times the room-temperature value but 12 to 13. The value of the phase-transition pressure was unchanged by this.

2) It is known, for example, that at atmospheric pressure $(TMTSeF)_2ClO_4$ remains a metal at all temperatures and even goes into the superconducting state at $T_c \approx 1$ K,[13] while the isostructural compound $(TMTSeF)_2PF_6$ is a dielectric at atmospheric pressure.[14]

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