the acoustic branch $p^2=\omega^2/c^2$ as the frequency ω increases.

4) In the more general boundary-value problem in which $\alpha_c \neq 0$, we should have in Eq. (33) in place of the single Bessel function $J_1(q_n r)$ the combination of two Bessel functions $AJ_1(q_n r) + BJ_1(q_n' r)$, where $q_n'^2 = q^2 - q_n^2$ is the second root of the biquadratic equation (34) for q_n^2. However, for $\alpha_c = 0$ such a combination satisfies the homogeneous boundary conditions (30) and (32) for $\Omega_c R = 0$ only if A or B vanishes.

[1] H. E. Hall, Proc. Roy. Soc. **245**, 546 (1958).
[2] H. E. Hall, Adv. Phys. **9**, 89 (1960).
[3] É. L. Andronikashvili, Yu. G. Mamaladze, S. G. Matinyan, and D. S. Tsakadze, Usp. Fiz. Nauk **73**, 3 (1961) [Sov. Phys. Usp. **4**, 1 (1961)].
[4] E. L. Andronikashvili and Yu. G. Mamaladze, Rev. Mod. Phys. **38**, 567 (1966).
[5] V. K. Tkachenko, Zh. Eksp. Teor. Fiz. **49**, 1875 (1965); **50**, 1573 (1966); **56**, 1763 (1969) [Sov. Phys. JETP **22**, 1282 (1966); **23**, 1049 (1966); **29**, 945 (1969)].
[6] H. E. Hall and W. F. Vinen, Proc. Roy. Soc. **A238**, 215 (1956).
[7] D. Stauffer, Phys. Lett. **A24**, 72 (1967).
[8] V. K. Tkachenko, Pis'ma Zh. Eksp. Teor. Fiz. **17**, 617 (1973) [JETP Lett. **17**, 434 (1973)].
[9] M. Ruderman, Nature **225**, 619 (1970).
[10] Dzh. S. Tsakadze and S. Dzh. Tsakadze, Pis'ma Zh. Eksp. Teor. Fiz. **18**, 605 (1973); Usp. Fiz. Nauk **115**, 503 (1975) [JETP Lett. **18**, 355 (1973); Sov. Phys. Usp. **18**, 242 (1975)].
[11] V. K. Tkachenko, Zh. Eksp. Teor. Fiz. **67**, 1984 (1974) [Sov. Phys. JETP **40**, 985 (1975)].
[12] É. B. Sonin, Zh. Eksp. Teor. Fiz. **69**, 921 (1975).
[13] L. Reatto, Phys. Rev. **167**, 191 (1968).
[14] I. M. Khalatnikov, Teoriya sverkhtekuchesti (The Theory of Superfluidity), Nauka, 1971.
[15] E. M. Lifshitz and L. P. Pitaevskiĭ, Zh. Eksp. Teor. Fiz. **33**, 535 (1957) [Sov. Phys. JETP **6**, 418 (1958)].
[16] S. V. Iordanskiĭ, Zh. Eksp. Teor. Fiz. **49**, 225 (1965) [Sov. Phys. JETP **22**, 160 (1966)].
[17] F. Dyson, Neutron Stars and Pulsars, Fermi Lectures, 1970. Roma, 1971 (Russ. Transl., Mir, 1973).
[18] I. L. Bekarevich and I. M. Khalatnikov, Zh. Eksp. Teor. Fiz. **40**, 920 (1961) [Sov. Phys. JETP **13**, 643 (1961)].
[19] G. A. Gamtsemlidze, Sh. A. Dzhaparidze, Ts. M. Salukvadze, and K. A. Turkadze, Zh. Eksp. Teor. Fiz. **50**, 323 (1966) [Sov. Phys. JETP **23**, 214 (1966)].

Translated by A. K. Agyei

Electric and magnetic properties of the organic metal TSeF-TCNQ

L. I. Buravov, R. N. Lyubovskaya, R. B. Lyubovskiĭ, and M. L. Khidekel'

Institute of Chemical Physics, USSR Academy of Sciences

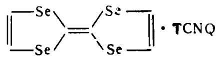
(Submitted December 11, 1975)
Zh. Eksp. Teor. Fiz. **70**, 1982–1986 (May 1976)

The temperature dependence of the conductivity in the microwave region and the magnetic susceptibility in the 1.5–300°K temperature interval are studied for the organic metal tetraselenafulvalene-tetracyanoquinodimethan (TSeF-TCNQ). The conductivity is maximal at temperatures 35–40°K at which it is from 7 to 20 times greater than at 300°K. The dielectric constant is $3 \cdot 10^4$ at $T = 4.2$°K. The gap calculated from the conductivity at low temperatures is identical with that derived from the susceptibility data. At high temperatures the resistivity can satisfactorily be described by a quadratic function of T.

PACS numbers: 72.30.+q, 72.15.Eb, 75.30.Cr

Great interest has been advanced recently in the study of organic salts based on tetracyanoquinodimethan (TCNQ), which have properties of quasi-one-dimensional metals.[1,2] These properties are determined principally by the composition and symmetry of the cation. It can now be regarded as established that such metallic properties are possessed by TCNQ salts of two types: the first type[3–7] are TCNQ salts with asymmetric cation, in which the Peierls instability of the one-dimensional metallic state is suppressed by the structural disorder, and the second type[8–11] comprises TCNQ salts with symmetrical cation, having conductivity along the cation and anion stacks. The suppression of the Peierls instability in salts of this type is apparently greatly weakened by the fact that the Peierls distortions are not commensurate with the period of the initial lattice, a situation resulting from the unequal distribution of the electrons among the cation and anion stacks.

Studies of TCNQ salts of the second type are presently diligently pursued, the symmetrical cation employed being tetrathiofulvalene (TTF)[10,11] and tetrathiatetracene.[8,9,12] In these complexes, the metallic state is stabilized in a wide temperature interval. The dc conductivity of the salt tetraselenafulvalene–tetracyanoquinodimethan (TSeF–TCNQ), which is isostructural with the salt TTF–TCNQ,[13] was recently investigated. In this study we investigate the temperature dependence of the conductivity of the same salt in the microwave band, as well as its magnetic susceptibility. The chemical formula of the salt is



The temperature dependence of the conductivity was measured at a frequency 10^{10} Hz by the contactless method described in[14], in the temperature interval 4.2–300 °K. For the conductivity measurements we

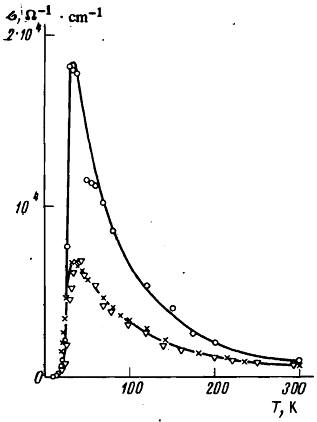


FIG. 1.

chose the thinnest needle-shaped crystals of thickness ~ 5 μ, since the calculation method of[14] can be used under the condition that the thickness of the skin layer is larger than or comparable with the thickness of the crystal. It was found that at room temperature the average value of the microwave conductivity, measured in three crystals, is $800 \pm 100\ \Omega^{-1}\ \text{cm}^{-1}$. The conductivity calculated from the dc data obtained by us by a four-contact method at room temperature is close to this value, $900 \pm 300\ \text{cm}^{-1}\ \Omega^{-1}$.

Figure 1 shows the temperature dependences of the microwave conductivities of three single crystals of the salt. On going from room temperature to 40 °K, the conductivity increases, reaching a maximum in the temperature interval 35–40 °K. The maximum value of the conductivity $\sigma_{\max}$ for different samples is 7–20 times larger than the conductivity at $T = 293$ °K. This discrepancy in values of $\sigma_{\max}$ for different samples is apparently due to the different number of defects in the crystals chosen from one and the same batch. With further decrease of the temperature, the conductivity decreases, with $\sigma_{4.2\,\text{K}} \approx 20\ \text{cm}^{-1}\ \Omega^{-1}$. The obtained data for the microwave conductivity are in good agreement with the results of Etemad *et al.*,[13] who investigated the temperature dependence of the dc conductivity of this salt. We have also determined the dielectric constant of this salt at 10^{10} Hz for the direction along the piles. It turned out to be much higher than in other investigated salts of the quasi-one-dimensional type,[15,16] and is equal to 3×10^4 at $T = 4.2$ °K.

The magnetic susceptibility of the complex TSeF–TCNQ was measured with the previously described[17] Faraday-type magnetic balance in the temperature interval 1.5–300 °K. The total measured susceptibility consists of four parts: the intrinsic susceptibility of the substance, consisting of diamagnetic and paramagnetic parts, and the susceptibility due to the paramagnetic and ferromagnetic impurities. In view of the different dependences of each of these parts on the magnetic field and on the temperature, they can be separated by measuring $\chi(T)$ in the temperature interval 1.5–300 °K and $\chi(H)$ at room temperature in the field interval 0.5–8.1 kOe.

In accordance with the rule of Honda and Owen, the measurement of the susceptibility as a function of the magnetic field makes it possible to separate the fraction of the ferromagnetic impurity $\chi_{\text{ferro}}(H)$. Analysis of the $\chi_{\text{meas}}(1/H)$ curve has shown that at room temperature $\chi_{\text{meas}} - \chi_{\text{ferro}} = 1.15 \pm 0.03\ \text{cm}^3/\text{mole}$. From the same curve we estimated the concentration of the ferromagnetic impurities in the sample referred to ferromagnetic iron, namely 14 parts in 10^6. This relatively large content of the ferromagnetic impurity is apparently due to the fact that the synthesis of the investigated complex was carried out in ordinary chemical vessels and no special measures were made to exclude absorption of impurities from the vessel wall.[18]

The cation in the investigated complex is symmetrical, and the low temperature dependence of its susceptibility differs substantially from the low-temperature susceptibility of the well-conducting TCNQ complexes with asymmetrical cations such as quinolinium, *N*-methyl-phenazinium, and others.[19] Whereas in complexes with asymmetric cations the low-temperature increase of the susceptibility is connected with the irregularity in the packing of the cation molecules in the pile and $\chi(T)$ varies with temperature like a meromorphic function,[1,19] in the case of TCNQ molecules with symmetrical cations no random potential is produced along the stacks of the TCNQ molecules and the negligible increase of the susceptibility at low temperatures is due to random defects and impurities. In this case the susceptibility should vary in accordance with the Curie law with a Curie constant determined by the degree of purification of the investigated compound. In our case the susceptibility varies in accordance with the Curie law in the temperature interval 1.5–16 °K, with a constant corresponding to a 0.1% paramagnetic impurity with $S = \frac{1}{2}$.

The value of the diamagnetic contribution to the measured susceptibility χ_{dia} was determined from the Pasqual rule. The value calculated in this manner is $\chi_{\text{dia}} = -2.3 \times 10^{-4}\ \text{cm}^3/\text{mole}$. Extrapolation of the low-temperature susceptibility plotted in coordinates $\chi(T)$ and $1/T$ to the coordinate axis at $1/T \to 0$ makes it possible to estimate independently the diamagnetic contribution to the total susceptibility. The value of χ_{dia} obtained in this manner is in relatively good agreement with the value calculated by Pasqual's rule and is equal to $-2.44 \times 10^{-4}\ \text{cm}^3/\text{mole}$.

After subtracting from the susceptibility measured with the balance all the foregoing contributions, we are left with the susceptibility χ_{para}, which corresponds to the intrinsic spin system of the investigated complex. Its dependence on the temperature is shown in Fig. 2. It is seen from Fig. 2 that starting with room temperature χ_{para} decreases monotonically all the way to 40–45 °K, after which it drops abruptly to zero.

The absence of a finite susceptibility at $T = 0$ °K indicates that below the transition temperature we are dealing with a nonmagnetic dielectric. In this respect, the investigated complex differs substantially from the well-conducting TCNQ salts with quinolinium, acridinium, and *N*-methylphenazinium, the ground state of which is a magnetic Mott insulator.[1,19] The energy gap of the TSeF–TCNQ complex can be determined from the tem-

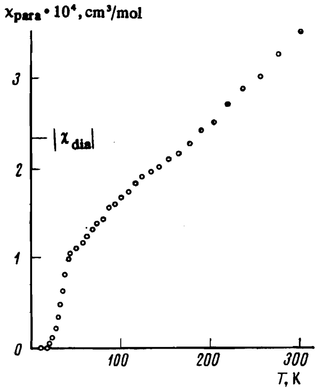


FIG. 2.

perature dependence of χ_{para} at $T < 40$ °K. The dependence of $\ln(\chi T)$ on $1/T$ in this temperature interval is linear and corresponds to a gap ~ 190 °K. The activation gap obtained from susceptibility data is 170 °K[18] for TTF–TCNQ and ~ 240 °K[8] for TTT–$(TCNQ)_2$.

It is seen from Fig. 1 that the conductivity reaches a maximum in the temperature region where an abrupt break occurs in the susceptibility. Below 35 °K the conductivity is of activation origin with a gap ~ 200 °K. The agreement between the gap calculated from the susceptibility and the gap connected with the conductivity allows us to state that at low temperatures we deal with a single-excitation from the valence band to the conduction band. Similar agreement between the activation energies takes place also in TTF–TCNQ.[18] In TTT–$(TCNQ)_2$ the gap obtained from the conductivity is much larger ($\Delta \sim 850$ °K) than the magnetic gap.[8] This may be due to penetration of the solid molecules into the lattice of the complex.

Above the maximum-conductivity temperature T_{cond} we attempted to describe the resistivity ρ of the complex TSeF–TCNQ by the binomial $\rho(T) = \rho_0 + \rho_2 T^2$. The curve plotted in coordinates $\rho(T)$ and T^2, for measurements on three samples taken from one and the same synthesized batch, are indeed well described by this formula in the temperature interval $T_{cond} < T < 250$ °K, but at lower temperatures they deviate downward, in contrast to the results of Etemad *et al.*[13] It should be noted that the value of ρ_2 measured with direct current[13] agrees well with our resistivity measurements in the microwave band, where $\rho_2 = (1.6 \pm 0.4) \cdot 10^{-8}$ Ω-cm/° K^2. This value of ρ_2 is quite close to the values obtained for ρ_2 in different laboratories for the salt TTF–TCNQ, so that we can state, first, that ρ_2 is apparently an intrinsic characteristic of these complexes and, second, that their conductivity at $T_{cond} < T$ is described by identical mechanisms. It should be noted, however, that an attempt to describe the conductivity of the salt TTT–$(TCNQ)_2$ by the same quadratic law ended in failure.

In conclusion, the authors thank I. F. Shchegolev for useful consultations and for constant interest in the work.

[1] F. Shchegolev, Phys. Status Solidi [a] 12, 9 (1972).
[2] M. L. Khidekel' and E. B. Yagubskiĭ, Usp. Khim. 16, 2132 (1972).
[3] L. N. Bulaevskiĭ, R. B. Lyubovskiĭ, and I. F. Tsegolev, Pis'ma Zh. Eksp. Teor. Fiz. 16, 42 (1972) [JETP Lett. 16, 29 (1972)].
[4] F. F. Iroshin, O. N. Eremenko, A. P. Kir'yanov, and I. F. Shchegolev, Pis'ma Zh. Eksp. Teor. Fiz. 19, 644 (1974) [JETP Lett. 19, 333 (1974)].
[5] V. N. Topnikov and I. F. Shchegolev, Pis'ma Zh. Eksp. Teor. Fiz. 20, 404 (1975) [JETP Lett. 40, 182 (1975)].
[6] F. F. Igoshin, A. P. Kir'yanov, V. N. Topnikov, and I. F. Shchegolev, Zh. Eksp. Teor. Fiz. 68, 1203 (1975) [Sov. Phys. JETP 41, 597 (1975)].
[7] L. N. Bulaevskiĭ, A. A. Gusseĭnov, O. N. Eremenko, V. N. Topnikov, and I. F. Shchegolev, Fiz. Tverd. Tela 17, 781 (1975) [Sov. Phys. Solid State 17, 498 (1975)].
[8] L. I. Buravov, O. N. Eremenko, R. B. Lyubovskiĭ, L. P. Rozenberg, M. L. Khidekel', R. P. Shibaeva, I. F. Shchegolev, and E. B. Yagubskiĭ, Pis'ma Zh. Eksp. Teor. Fiz. 20, 457 (1974) [JETP Lett. 20, 208 (1974)].
[9] O. N. Eremenko, M. L. Khidekel', D. N. Fedutin, and E. B. Yagubskiĭ, Izv. Akad. Nauk SSSR Ser. Khim. 4, 984 (1972).
[10] D. O. Ferraris *et al.*, JACS 95, 948 (1973).
[11] L. B. Coleman *et al.*, Solid State Commun. 12, 112 (1973).
[12] P. Delhaes, S. Flandrois, G. Keryer, and P. Dupuis, Mater. Res. Bull. 10, 825 (1975).
[13] S. Etemad. T. Penney, E. M. Engler, B. A. Scott, and P. E. Seiden, Phys. Rev. Lett. 34, 741 (1975).
[14] L. I. Buravov and I. F. Shchegolev, Prib. Tekh. Eksp. 2, 171 (1971).
[15] A. S. Berenblyum, L. I. Buravov, M. L. Khidekel', I. F. Shchegolev, and E. B. Yakimov, Pis'ma Zh. Eksp. Teor. Fiz. 13, 619 (1971) [JETP Lett. 13, 440 (1971)].
[16] S. K. Khanna, A. F. Garito, and A. J. Heeger, Solid State Commun. 16, 667 (1975).
[17] R. B. Lyubovskiĭ and I. F. Shchegolov, Prib. Tekh. Éksp. No. 5, 231 (1968).
[18] J. S. Scott, A. F. Garito, and A. J. Heeger, Phys. Rev. [B] 8, 3131 (1974).
[19] L. N. Bulaevskiĭ, A. V. Zvarykina, Yu. S. Karimov, R. B. Lyubovskiĭ, and I. F. Shchegolev, Zh. Eksp. Teor. Fiz. 62, 725 (1972) [Sov. Phys. JETP 35, 384 (1972)].

Translated by J. G. Adashko