Structure and electromagnetic properties of a new high-conductivity complex $(TTT)^+(TCNQ)_2^-$

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The complex $(TTT)(TCNQ)_2$ contains two types of conducting chains —cation and anion. The conductivity of the complex is metallic up to 90 °K, after which it decreases rapidly. The temperature dependence of the susceptibility offers evidence of a transition into the state of a diamagnetic dielectric at 55–60 °K.

1. Compounds that contain simultaneously conducting chains of various types (e.g., cation and anion radicals) are of great interest because they uncover new possibilities of stabilizing the one-dimensional metallic state and eliminating the influence of defects. The first representatives of compounds of this type, ion radicals such as tetracyanoquinodimethan (TCNQ) with the cation radical tetrathiotetracene (TTT), were described in[1]. We wish to present here data on the structure of the complex $(TTT)^+(TCNQ)_2^-$ and its electric and magnetic properties.

2. The crystals of the complex (dark-violet needles of length ~3—6 mm) were obtained by cooling a reaction mixture containing a solution of TTT and TCNQ in chlorobenzene or nitrobenzene. The cooling was carried out at a rate of ~1° per hour from 50 to 20 °C. The reaction took place in a quartz vessel in an atmosphere of argon. The initial TCNQ was triply purified by recrystallization from acetonitryl and by double vacuum sublimation in a quartz sublimator, where the initial TTT was purified by double vacuum sublimation. According to the EPR data, the content of the paramagnetic impurities after purification did not exceed 0.01% in the TCNQ and 0.2% in the TTT.

An elemental analysis has shown that the complex contains a certain amount of solvent, which varies from synthesis to synthesis and apparently from crystal to crystal. For this reason, most crystals are strongly disordered, and only some of them are suitable for an x ray experiment. Examination of the structure of such crystals did not reveal the presence of solvent in them.

The main crystallographic parameters of the complex are $a=19.152$, $b=12.972$, and $c=3.754$ Å; $\alpha=88°28'$, $\beta=91°43'$, $\gamma=71°44'$; $V=901.23$ Å^3; $Z=1$, and $d_{calc}=1.41$ g/cm^3; the space group is $P1$. The structure was determined from an analysis of the three-dimensional Patterson function and refined by least squares in the isotropic approximation to $R=0.125$ (1686 reflections, DAR-UM diffractometer).

A characteristic feature of the structure is the presence of isolated cation and anion stacks proceeding along the c axis (Fig. 1). The interplanar TCNQ—TCNQ and TTT—TTT distances are 3.18 and 3.52 Å respectively. The angle between the normals to the planes of the TCNQ and TTT molecules is 15°. The TCNQ molecules in the stack overlap in the same manner as in all high-conductivity TCNQ complexes. The overlap of the TTT

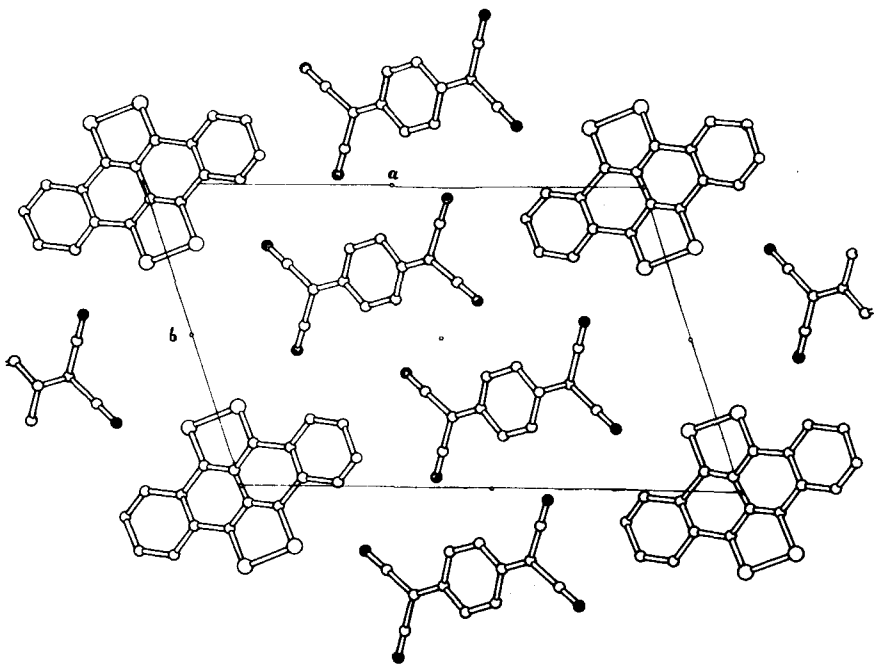

FIG. 1. Projection of the structure along the c axis.

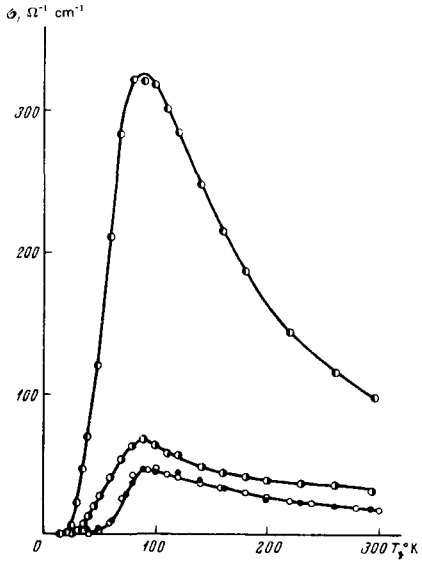

FIG. 2. Temperature dependences of the microwave conductivity of four different crystals of the $(TTT)(TCNQ)_2$ crystal.

molecules, 2.083 Å, is equal to half the interatomic $S-S$ distance.

4. The temperature dependence of the dc conductivity differs greatly in different crystals, and most measurements cannot be duplicated even in the same single crystal because of the tendency of the crystal crack upon cooling. We therefore present only the results of measurements of the conductivity by a contactless method at a frequency 10^{10} Hz, which were carried out in the temperature interval 4.2–300 °K with the installation of[2].

Figure 2 shows the temperature dependence of the microwave conductivity in the direction of the c axis for four out of the 19 investigated crystals of the complex. A characteristic feature of the curves is the presence of a maximum at 90 °K. The ratio $\sigma_{max}/\sigma_{room}$ varies from crystal to crystal in the range from 2 to 3.5, the room-temperature conductivity ranges from 20 to 160 $\Omega^{-1}\,cm^{-1}$, and the dielectric constant at 4.2 °K varies from 300 to 1800.

5. The static magnetic susceptibility was measured by the Faraday method in the temperature interval 1.5–360 °K in fields from 0.5 to 9 kOe. The concentration of the ferromagnetic impurities in the samples, estimated from an analysis of the dependence of χ on $1/H$, did not exceed 10^{-6} when recalculated in terms of iron. In the temperature region 1.5–25 °K, the susceptibility agrees excellently with the Curie law, with a constant corresponding to a content of 2 to 4% localized spins with $S=1/2$. Such a large concentration of the localized spins, which furthermore varies from synthesis to synthesis, is obviously due to peculiarities in the penetration of the solvent molecules into the lattice of the complex.

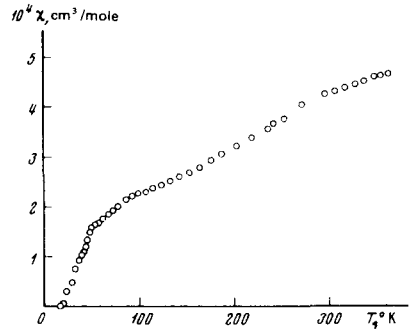

FIG. 3. Temperature dependence of the paramagnetic susceptibility.

Figure 3 shows the temperature dependence of the paramagnetic susceptibility of the complex, obtained after subtracting the impurity contribution. At high temperatures, χ tends to a constant value 4.7×10^{-4} cm^3/mole. With decreasing temperature, it first decreases monotonically, and then vanishes rapidly after 55–60 °K.

6. At the present time, the most important problem in the development of quasi-one-dimensional metallic systems is that of stabilizing the high-temperature metallic state. Of definite interest in this respect are compounds that contain conducting chains of various types. It can be assumed that the resultant complication of the band structure will contribute to some degree to the weakening of various types of instabilities.

The investigated complex is just to this type, as is the well-known complex (TTT)(TCNQ).[3,4] The difference between them is that the initial one-dimensional bands of the TCNQ chains are filled differently in them, to 1/4 in $(TTT)(TCNQ)_2$ and to 1/2 in (TTF)(TCNQ). However, the behaviors of the complexes have much in common. Just as (TTF)(TCNQ), the complex $(TTT)(TCNQ)_2$ goes over into the state of a diamagnetic dielectric at 55–60 °K, except that the maximum of the conductivity is not so appreciable here and occurs at a somewhat higher temperature. The latter circumstance can, incidentally, be connected with the influence of the disorder that results from the penetration of the solid molecule into the lattice of the complex.

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