

MECHANISM OF CONDUCTIVITY OF WELL-CONDUCTING COMPLEXES ON THE BASIS  
OF TETRACYANQUINODIMETHYL

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The temperature dependence of the conductivity of two single-crystal highly conducting ( $\sigma_{290^\circ\text{K}} = (0.7 \pm 0.3) \cdot 10^2 \text{ ohm}^{-1}\text{-cm}^{-1}$ ) organic complexes based on tetracyanquinodimethyl (TCQM) is investigated at temperatures between 10 and 300°K. The complexes are (TCQM)<sub>2</sub> quinoline (I) and (TCQM)<sub>2</sub> acridine (II). The conductivities are maximal at 240 and 140°K for I and II, respectively. At lower temperatures, the conductivity depends exponentially on the inverse temperature, the activation energies being 340 and 240°K for complexes I and II, respectively. The temperature dependence of the thermal emf is measured between 30 and 300°K for complexes I, II, (TCQM)<sub>2</sub> thiazolinocarbocyanine (III) and (TCQM)N-methylphenazine (IV). The conductivity measurements were carried out with polycrystalline samples as well as with single crystals (for the complexes II and IV). The behavior of the polycrystalline samples was found to differ weakly from that of the single crystals. For all the investigated compounds, the sign of the thermal emf corresponded to electronic conductivity. Possible explanations of the observed temperature variation of the conductivity are discussed. It is shown that the behavior of the thermal emf can apparently be explained most simply within the framework of the almost-localized carrier model.

**H**IGHLY conducting complexes on the basis of tetracyanquinodimethyl (TCQM)<sup>[1,2]</sup> are the best of the known organic conductors of electricity, apart from graphite. Their conductivity in the direction along the stacks of the TCQM molecules reaches  $10^2 \text{ ohm}^{-1} \text{ cm}^{-1}$  at room temperature. A study of these complexes is of definite interest in connection with Little's idea<sup>[3]</sup> of the possibility of a non-phonon superconductivity mechanism in organic compounds. Were these complexes to have a conductivity of the metallic type, as was stated in the early papers<sup>[1,2]</sup>, they would be ideal initial objects for attempts at synthesizing organic superconductors<sup>[4]</sup>.

Yet at the present time little is known concerning the conductivity mechanism of these complexes. One of the causes of such a situation is that many physical effects in these substances cannot be measured (for example galvanomagnetic and thermomagnetic effects, the Hall effect, and the photoeffect); such effects would make it possible to obtain in simple fashion the information needed for this purpose. On the other hand, there are practically no data on measurements, made in single crystals of highly-conducting compounds of this class of the temperature dependence, of such measurable quantities as the conductivity and the Seebeck effect. This is apparently due to the fact that it is impossible to grow sufficiently large single crystals of such complexes. The measurements are performed as a rule on pressed tablets and therefore cannot be regarded as sufficiently representative.

We have investigated the temperature dependence of the conductivity and of the thermal emf of a number of well-conducting TCQM complexes. We measured the conductivity of single crystals of the complexes (TCQM)<sub>2</sub> quinoline (I) and (TCQM)<sub>2</sub> acridine (II) in the temperature interval 10–300°K. The thermal emf was

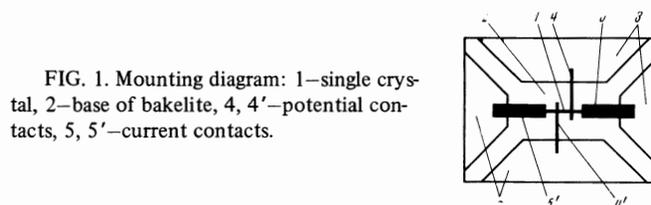


FIG. 1. Mounting diagram: 1—single crystal, 2—base of bakelite, 4, 4'—potential contacts, 5, 5'—current contacts.

measured in the temperature interval from room to 30–40°K. At lower temperatures, measurements are practically impossible because of the high resistance of the samples. Here, in addition to the two aforementioned complexes, we investigated also the complexes (TCQM)<sub>2</sub>-thiazolinocarbocyanine (III) and (TCQM)N-methylphenazine (IV). The data on the temperature dependence of the conductivity of single crystals of the complex IV were published by us earlier<sup>[5]</sup>.

## I. STUDY OF THE TEMPERATURE DEPENDENCE OF THE CONDUCTIVITY

### 1. Experiment

The measurements were performed with direct current using a four-contact null method. The investigated crystals were in the form of needles of 5–15  $\mu$  diameter and 2–2.5 mm long. The electric conductivity of the relatively poorly-conducting complexes of TCQM, which are available in the form of relatively large crystals, is strongly anisotropic<sup>[1,6,7]</sup>; the same anisotropy exists apparently also in the well-conducting complexes. We measured the conductivity in the direction of the long dimension of the crystal, corresponding to the direction of maximum conductivity.

The sample mounting is shown in Fig. 1. The

crystal was glued to a bakelite base 2 on which four strips of metal foil 3, insulated from one another, were glued. Four silver current leads (4, 4', 5, 5') providing the electric contact between the crystal and the copper strips, were sputtered onto the base with the crystal through an appropriate mask. The insulation resistance between any two silver electrodes exceeded  $10^{12}$  ohm and introduced no noticeable errors in the measurement results at any temperature.

When the crystal was firmly glued, the difference between the coefficients of linear expansion of the crystal and the base caused the crystal to break when the temperature was lowered. We therefore used as the glue the low-volatility inert oil GKZh-94, which has a low freezing temperature ( $\sim 200^\circ\text{K}$ ). With such a mounting, the investigated samples could be cooled down to helium temperatures, and succeeding cooling cycles did not lead to changes in their properties.

The base with the sample was placed in a helium Dewar. The measurements were carried out with the sample temperature raised from that of liquid helium. The regulation and stabilization of the temperature were effected with the aid of a heater wound on a bulky copper container surrounding the sample. The copper shell was connected to the helium bath by a cold finger, making it possible to establish the required temperature. The temperature was measured with the aid of a Cu-Au + 0.07% Fe thermocouple, one junction of which was pressed against one of the copper strips 3, while the other was kept at  $0^\circ\text{C}$ . The temperature measurement accuracy was not worse than  $\pm 1\%$ .

The measuring current flowing through the sample did not exceed  $1 \mu\text{A}$  at any temperature, reaching  $0.01 \mu\text{A}$  at the lowest temperatures. The voltage between the potential contacts was measured with the aid of an R-306 potentiometer and F-116 galvanometer as a null instrument. The relative resistance-measurement error did not exceed  $\pm 1\%$  in this case.

## 2. Results and Discussion

The temperature dependences of the conductivities of the complexes I and II are shown in Figs. 2 and 3, respectively. Owing to the inaccuracy with which the transverse dimensions of the crystals were determined, the scatter in the absolute values of the conductivity, measured for different crystals of the same complex, can reach  $\pm 50\%$ . At the same time, the scatter of the relative values of  $\sigma(T)/\sigma(290^\circ\text{K})$  does not exceed  $1\%$ , as can be seen from the plots in Figs. 2 and 3, which show data for several different single crystals of the corresponding complexes.

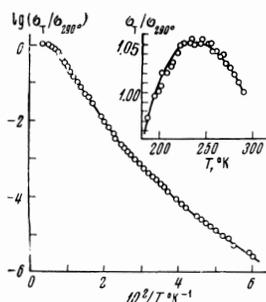


FIG. 2. Temperature dependence of the conductivity of a single crystal complex I.

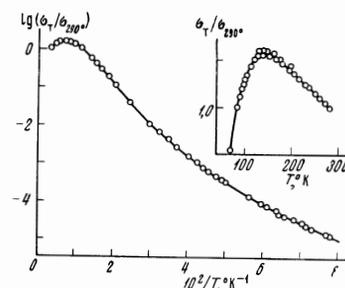


FIG. 3. Temperature dependence of the conductivity of a single crystal of complex II. In the insert, one division on the ordinate axis is equal to 0.5.

The room-temperature conductivities of both investigated complexes, according to the measurements on seven different crystals of each complex, is the same within the limits of measurement accuracy and is equal to  $(0.7 \pm 0.3) \times 10^2 \text{ ohm}^{-1} \text{ cm}^{-1}$ . With decreasing temperature, the conductivity first increases, reaching a maximum at  $240^\circ\text{K}$  for complex I and at  $140^\circ\text{K}$  for complex II. With further lowering of the temperature, it begins to decrease in accordance with a law close to exponential in the reciprocal temperature, with activation energies  $340$  and  $240^\circ\text{K}$  respectively for the complexes I and II. At the lowest temperatures, this decrease again slows down, indicating a decrease in the activation energy.

We note that the conductivity of the compressed tablets at room temperature is smaller by approximately two orders of magnitude, and reveals no increase whatever with decreasing temperature; it begins to decrease immediately with approximately the same activation energies as for the single crystals.

The observed temperature dependence of the conductivity shows unambiguously that we are dealing with semiconducting compounds, and the question is what factor determines mainly the change of conductivity with temperature: is it due to the change in the carrier density or to changes in the mobility? In the former case, to describe the properties of the investigated class of compounds it would be possible to use ordinary band concepts, which have been sufficiently thoroughly developed. In the latter case, the motion of the carriers at any particular stage must include of necessity a thermally activated jump.

Of course, data only on the temperature dependence of the conductivity do not suffice to answer this question. In an earlier paper<sup>[5]</sup> we attempted to compare the temperature dependence of the conductivity with the temperature dependence of the susceptibility of the complex IV within the framework of the band concepts. It turned out in this case that the variation of the conductivity with temperature cannot be attributed to a change in the carrier density. And since in the band scheme the mobility cannot have as strong a temperature dependence as would be required to explain the observed variation of the conductivity, it was necessary to assume that the mobility is limited by potential barriers produced by defects and distortions in the linear conducting chain of TCQM molecules.

A similar analysis with the same results can be carried out also for the complexes I and II, the suscep-

tibilities of which depend on the temperature in analogous fashion<sup>[2]</sup>. The main assumption in this case, as before, is that the magnetic susceptibility of the complexes is due to the same electrons which determine also their electric properties. The close correlation between the electric and magnetic properties of highly different TCQM complexes, a correlation noted already in the earlier investigations<sup>[1,2]</sup> makes this assumption sufficiently likely.

Thus, apparently the only method of explaining the observed electric and magnetic properties of the well-conducting complexes of TCQM, using band concepts, is to assume that the linear chain of the TCQM molecules consists of sections having more or less good conductivity, separated by more or less appreciable potential barriers. Simple estimates show, however, that in this case the defect concentration  $c$  must be unreasonably high in order to explain the observed value of the conductivity.

In fact, if we neglect effects of tunneling and above-the-barrier reflection, then the conductivity of a single barrier in a one-dimensional chain can be estimated by means of the formula  $\sigma_1 = ne^2d/\pi\hbar(1 + e^{\varphi/kT})$ , where  $n$  is the number of filaments per unit area,  $d$  the linear dimension of the barrier,  $\varphi$  its height above the chemical-potential level. The measured conductivity is  $\sigma = \sigma_1/c$ , and if we assume  $d \sim 3 \times 10^{-8}$  cm (the distance between the TCQM molecules in the chain), we obtain  $c \sim 10\%$ .

## II. STUDY OF THE TEMPERATURE DEPENDENCE OF THE THERMAL emf

### 1. Experiment

For the complexes I and III, the measurements were performed on pressed tablets of 5 mm diameter; the complexes II and IV were in the form of rather long (on the order of several millimeters) single-crystal needles. This made it possible, besides performing the measurements on the tablets, to perform also measurements of the thermal emf along the long axis of the single crystals.

As the temperature pickups we used copper-constantan thermocouples welded together of wires 0.1 mm in diameter. Prior to the welding, the constantan wire was tested for thermoelectric homogeneity, and the most homogeneous pieces were chosen for the construction of the thermocouples. The accuracy with which  $\Delta T$  was measured was  $\sim 0.5\%$  down to the temperature of liquid nitrogen, and  $\sim 2-3\%$  below this temperature. We used a type R-306 potentiometer for the measurements. The measurements were performed at several differences  $\Delta T$ , and led as a rule to identical results.

A. Measurements on tablets. A tablet of the investigated substance with silver-coated ends was compressed by a spring between two cylindrical electrodes centered by a rigid teflon mount. On the contact planes of the copper electrodes, grooves were cut to hold the junctions of the measuring thermocouples. To eliminate a possible measurement error due to heat conduction via the thermocouple leads, the thermocouple was passed through a narrow hole drilled

parallel to the contact surface of the electrode. To ensure good thermal contact between the copper electrode and the thermocouple, the latter was glued with BF-2 adhesive, which was subsequently polymerized.

A controllable temperature gradient along the sample and regulation of the average temperature were effected by two heaters—flat spirals glued to the non-contact flat surfaces of the copper electrodes. Particular attention was paid to the quality of the thermal contact between the copper electrodes and the tablet.

B. Measurements on single crystals. The single crystals of the complexes, whose ends were coated with silver by vacuum sputtering, were placed on the base in such a way that they were tangent to the junctions of the measuring thermocouples. The contacts between the single crystals in the junctions were then covered with silver paste, and the thermal emf of the sample was measured between the copper branches of the thermocouples.

The difference between the temperature coefficients of expansion of the base and the crystal usually leads to breaking of the crystal or to deterioration of the contacts when the temperature is lowered. We were able to avoid this by using as the base an insulator-coated tablet of the same substance as the single crystals on which the measurements were made. The accuracy of the measurement results, estimated from the scatter of the data obtained with different single crystals of the same complex, was about  $\pm 10\%$ .

### 2. Measurement Results

The measurement results are shown in Figs. 4–7. For all the investigated complexes, the sign of the thermal emf at room temperature corresponds to electronic conductivity. Attention is called to the fact that the behavior of the thermal emf is similar for all three complexes of the salts: when the temperature drops down to 100–150°K, the value of  $\alpha$  first changes little or remains practically unchanged and only at lower temperatures does it begin to decrease rapidly. After this, the thermal emf is practically the same for all the complex salts in the region where  $\alpha$  changes little, and its average value is  $60 \mu\text{V}/\text{deg}$ <sup>1)</sup>. We note also that the behavior of the thermal emf of single crystals differs only insignificantly from the behavior of the thermal emf of polycrystalline samples<sup>2)</sup>.

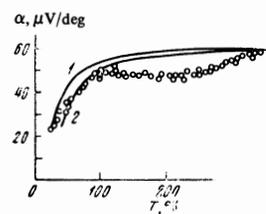


FIG. 4. Temperature dependence of the thermal emf of complex I. The solid curves are constructed in accordance with formula (1): curve 1— $\Delta J = 70^\circ\text{K}$ , curve 2— $\Delta J = 100^\circ\text{K}$ .

<sup>1)</sup>In essence, a similar behavior of the thermal emf of the complex I was observed also in [1].

<sup>2)</sup>The possible cause of the relatively large difference between the values for the single crystals and tablets of complex IV at low temperatures is discussed below, at the end of Sec. 3 of Ch. II.

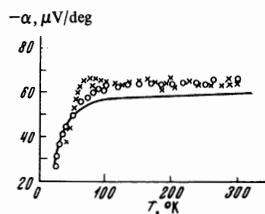


FIG. 5. Temperature dependence of the complex II: X—single crystals, O—polycrystalline sample. Solid curve constructed in accordance with formula (1) for  $\Delta J = 50^\circ\text{K}$ .

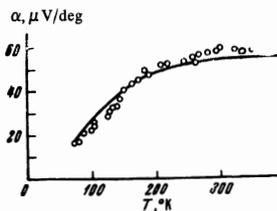


FIG. 6. Temperature dependence of the thermal emf of complex III. The solid curve is constructed in accordance with (1) for  $\Delta J = 230^\circ\text{K}$ .

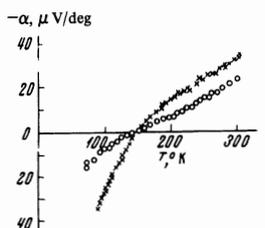


FIG. 7. Temperature dependence of the thermal emf of complex IV: X—single crystals, O—polycrystalline sample.

All this gives grounds for hoping that the obtained values, at least in the main, reflect the intrinsic properties of the investigated compounds and are not connected with various impurities or imperfections, to which the thermal emf is usually very sensitive.

We also attempted to observe transverse thermal magnetic effects in the investigated compounds. Within the limits of the measurement errors, a magnetic field of 7 kOe had no effect whatever on the value of the thermal emf.

### 3. DISCUSSION

The discussion carried out in Sec. 2 of Ch. I shows that the observed electric and magnetic properties of highly-conducting complexes of TCQM cannot be readily explained with the aid of usual band concepts. Moreover, from the point of view of the usual band scheme, it is also difficult to understand the aforementioned "representativeness" of the thermal electric properties of complex salts. In fact, the absolute magnitude of the thermal emf in these compounds is low. This should mean that we are dealing either with intrinsic or with well-compensated semiconductors. In either case, the magnitude and the behavior of the thermal emf should depend strongly on the amount and nature of the impurities, defects, etc., as is usually observed in objects of this kind. The identity of the thermoelectric properties of three different complex salts would appear to be, from this point of view, a highly improbable accident. At the same time, as we shall show now, a very simple model of a linear chain with localized carriers, moving from site to site via thermodynamically activated jumps, gives a satisfactory description of the observed behavior of the thermal emf.

The general thermodynamic expression for the thermal emf coefficient is<sup>[8]</sup>

$$\alpha = -(k/e)(Q - \mu) / kT,$$

where  $Q$  is the transport heat, i.e., the average energy transported by an electron current of unit density, and  $\mu$  is the chemical potential of the system of electrons.

Let us consider first the case of complex salts, when on the average there is one electron for every two sites. We assume that there can be no more than one electron per site, and the total energy of the system is made up additively of the energies  $J_\nu$  of the individual "bonds," characterized by the number of empty sites  $\nu$  located between two carriers. It is clear that  $J_\nu$  should decrease with increasing distance between electrons, and we neglect all  $j_\nu$  with  $\nu \geq 2$ .

Then the problem reduces to a calculation of the average energy and the chemical potential of a one-dimensional lattice gas, the energy of which can assume the values

$$E\{n_i\} = -J_0 \sum_i n_i n_{i+1} - J_1 \sum_i n_i (1 + n_{i+1}) n_{i+2},$$

where the summation is carried out over all the sites, with  $n_i = 0$  if the site is empty and  $n_i = 1$  if it is occupied by an electron. We do not take into account the dependence of the energy on the spin variables, because in the temperature interval of interest to us the magnetic susceptibility of the highly-conducting TCQM complexes is practically independent of the temperature<sup>[2,5]</sup>, thus offering evidence of the quenching of the spin degrees of freedom.

At  $kT \ll J_0$  we obtain

$$\alpha = -(k/e) [\ln(1 + e^{\beta \Delta J}) - \beta \Delta J e^{\beta \Delta J} / (1 - e^{\beta \Delta J})]$$

where  $\Delta J = J_1 - J_0$  and  $\beta = 1/kT$ . As seen from Figs. 4–6, where the solid lines represent the results of the calculations, by varying only one parameter  $\Delta J$  it is possible to describe satisfactorily the magnitude and temperature behavior of the thermal emf coefficient of all three complex salts.

The foregoing considerations cannot be used directly to explain the thermoelectric properties of the simple salt IV. In this case each TCQM molecule carries one electron, and doubly-charged ions of TCQM, the formation of which was assumed to be highly unfavored from the energy point of view, should arise when the electrons jump from site to site.

It should be noted, however, that the considered simple phenazine salt is unique in the value of its conductivity among all the known simple TCQM salts, which as a rule have low conductivity. It can therefore be assumed that it is precisely for this compound that the formation of doubly charged ions is greatly facilitated for some reason, at least at high temperatures. The statistical properties of the system will in this case be in essence the same as for complex salts, and one can understand the behavior of the thermal emf observed at high temperatures if it is assumed that the formation of doubly charged ions is nevertheless more difficult, even in such a simple model, than the production of a pair of neighboring electrons in the case of complex salts (so that the corresponding energy difference is still larger here).

In order to understand the reversal of the sign of

the coefficient of the thermal emf of the complex IV at low temperatures, it is necessary apparently to take into account the fact that certain TCQM molecules in the chain can give up their electrons to some centers with strong acceptor properties and thus turn out to be electrically neutral. At low temperatures, when it is practically impossible to produce doubly-charged ions, the conductivity is ensured only by the presence of such neutral molecules in the chain, and the partition function will be determined simply by the number of ways in which it is possible to place  $N_0 - N$  neutron molecules in  $N_0$  sites:  $Z = N_0! / (N_0 - N)! N!$ . This yields  $\mu/kT = -\ln[(N_0 - N)/N]$ , leading to  $\alpha > 0$ .

It is possible that the relatively large differences observable at low temperatures, when the thermal emf becomes positive between the values of the thermal emf of single crystals and polycrystalline samples of the complex IV are indeed explained as being due to such "impurity" character of this quantity.

In conclusion, we are sincerely grateful to M. L. Khidekel' and E. B. Yagubskii for supplying the substances for the investigation, to G. M. Éliashberg for

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129