# Metal-dielectric transition in the (NMP)(TCNQ) complex

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A phase transition, manifesting itself in a discontinuity of the specific heat at a temperature of 7.2°K, is observed in the (NMP)(TCNQ) complex. A detailed investigation of the transmission spectra of submillimeter radiation, carried out in the frequency interval 4–65 $\text{cm}^{-1}$ and at temperatures from 4 to 35°K, indicates that this transition is of the metal-dielectric type with distinctive features characteristic of the one-dimensional case.

## 1. INTRODUCTION

From the point of view of band representations, the quasi-one-dimensional electronic system of the complex (NMP) (TCNQ)1) is metallic with a half-filled conduction band. However, the temperature dependence of the conductivity of this complex has a metallic nature only at temperatures above 220°K, after which the conductivity rapidly falls with decreasing temperature.[1] In[2] such behavior of the conductivity was interpreted as one of the evidences for the transition of the complex into a dielectric state in the neighborhood of 200°K. On the other hand, it was noted in[3] that the decrease of the conductivity at low temperatures still does not necessarily indicate a loss of the metallic properties. It may be related to the internal degree of disorder inherent in this complex,[4] which is due to the asymmetry of the NMP cation.

The analysis of the electric and magnetic properties of the complex, which was carried out in[5], showed that it apparently remains actually in a metallic state down to temperatures of the order of 20 to 30°K, and only for temperatures below 10°K can its properties be interpreted as the properties of a one-dimensional, disordered Mott-Hubbard dielectric. The existence below 15°K of a gap in the electronic excitation spectrum of (NMP)(TCNQ), observed from an analysis of the transmission spectra of submillimeter radiation, was reported in[6].

In the present article we report on the observation of a phase transition in the complex (NMP)(TCNQ), which manifests itself in a discontinuity of the specific heat at a temperature of 7.2°K. A detailed investigation of the frequency dependence of the transmission coefficient for submillimeter radiation, carried out in the frequency interval 4–65 $\text{cm}^{-1}$ and at temperatures from 4.2 to 35°K, indicates that this transition is of the metal-dielectric type with distinctive features characteristic of the one-dimensional case.

## 2. TEMPERATURE DEPENDENCE OF THE SPECIFIC HEAT

a) Measurement procedure. The specific heat of the complex was measured with the aid of the low-temperature adiabatic calorimeter described in[7]. Measurements were made in the temperature interval 1.5–13.5°K. The sample was represented by a pellet of mass 0.996 g, pressed into a short copper heat conductor, which was connected with a thermometer and with a heater. For temperatures above 4.5°K the contribution of the "empty" calorimeter to the total heat capacity did not exceed 15 to 20%; it is described well by a combination of linear and cubic terms over the entire range of temperatures. Processing of the experimental data was run on a BÉSM-6 electronic computer.

b) Results of the measurements. The temperature dependence of the specific heat of the complex in the interval from 4.5 to 11°K is plotted in logarithmic coordinates in Fig. 1. The characteristic feature of this curve is the presence of a discontinuity in the specific heat at a temperature of 7.2°K. The magnitude of the discontinuity amounts to 6.5% of the value of the complex's specific heat at this point and exceeds by far the random error of the measurements, which does not exceed 0.5%.

Unfortunately, neither before nor after the discontinuity is it possible to approximate the behavior of the specific heat by any kind of simple law that would allow one to extrapolate over the entire temperature interval and thereby isolate the regular part of the curve. We further note that the behavior of the specific heat is smooth in the intervals 1.5–4.5 and 11–13.5°K.

## 3. TEMPERATURE DEPENDENCE OF THE OPTICAL TRANSMISSION SPECTRA FOR SUBMILLIMETER RADIATION

a) Measurement procedure. The radiation transmission coefficient was measured in the frequency interval 4–65 $\text{cm}^{-1}$ and in the temperature interval 4.5–35°K. The measurements were made with the aid of a single-beam echelette spectrometer, assembled according to the Czerny-Turner design. A PRK-4 mercury lamp served as the radiation source. The radiation was modulated at a frequency of 700 Hz by a mechanical chopper and was registered by an n-InSb detector, located at the end of a stainless-steel light pipe of 10 mm diameter. The light pipe was located in a transfer helium dewar, so that the detector always operated at 4.2°K.

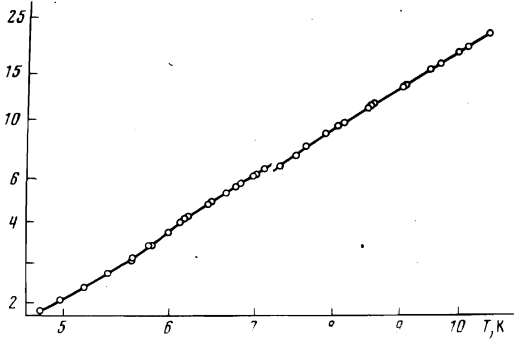

FIG. 1. Temperature dependence of the specific heat of the complex (NMP)(TCNQ), demonstrating the existence of a discontinuity at 7.2°K.

After synchronous detection, the signal was recorded by an automatic recording instrument. The receiver sensitivity in the working frequency band, at a 1 Hz bandwidth, amounted to $5 \times 10^{-12}$ W. In the absence of the sample, this ensured a signal/noise ratio of not less than 500.

The working wavelength band was covered by a set of echelettes with steps of 0.5, 0.85, 1.5, 2.5, and 3.5 mm with a groove-face angle of 15°. Filtration of the undesirable short wavelength radiation was achieved by the use of two filtering echelettes with steps twice as small as the working echelette, and filters of black paper and Mylar. The resolving power of the instrument, for input and exit apertures of 5 and 10 mm, amounted to 2.5 and 5%, respectively, upon operation near the blaze angle. Calibration of the monochromator and verification of the purity of the spectrum were carried out with the aid of a Michelson interferometer.[8]

Compact samples of the complex, even of small thickness, transmitted practically no radiation in the employed range of frequencies and temperatures. The samples used in the measurements were therefore suspensions of the investigated complex in paraffin with weight concentrations 1–3%. They were prepared by a thorough grinding of the two components together in a mortar, into which a small amount of liquid nitrogen was poured, and subsequent pressing of the resulting powder into pellets of 10 mm diameter and of thickness 1 to 2 mm. The dimensions of the complex's particles were different in the sample, but did not exceed ten microns.

The pellets, in a thin brass clip, were placed in the light pipe ahead of the submillimeter radiation detector. The temperature of the samples was regulated by their displacement in the light pipe and was measured by a Cu–Cu + 0.12% Fe thermocouple soldered to the clip. The transmission coefficient was found as the ratio of the intensity of the radiation passing through the sample to the intensity of the radiation incident on the detector in the absence of the sample.

b) Results of the measurements. An exact analysis of the interaction of radiation with matter in the composite samples employed in our experiments is extremely complicated. However, one can present the following considerations, enabling one to establish a connection between the measured transmission coefficient and the properties of the investigated complex of interest to us.

The dimensions of the complex's particles in the sample are small ($\lesssim 10\ \mu$) in comparison with the radiation wavelength ($\lambda_{\min} = 150\ \mu$). Therefore, diffuse scattering of the radiation by the particles of the complex can be neglected. Furthermore, as our measurements showed, intrinsic absorption in the paraffin is negligible in the frequency and temperature ranges under investigation. Therefore, the transmission coefficient $\tau$ can be represented with sufficient accuracy in the form

$$\tau=(1-R)^2\exp(-n\Sigma d),$$

where R is the energy-dependent coefficient of reflection from the surface of the sample, d is the sample thickness, n is the concentration of particles of the complex, and $\Sigma$ is the effective cross section for the absorption of radiation, averaged over all particles.

Generally speaking the reflection coefficient R is determined by the properties of the paraffin as well as by the properties of the complex's particles suspended in it; however, for small concentrations of the latter the quantity R will be small. Therefore, the frequency dependence of log $(1/\tau)$ will essentially duplicate, in its principal features, the frequency dependence of the effective cross section for the absorption of radiation by the particles of the complex.

The corresponding experimental results are shown in Fig. 2, on which the frequency dependence of log $(1/\tau)$ is plotted at various temperatures. For the sake of convenience, all of the curves in this figure are attached at 4 $\text{cm}^{-1}$ to one and the same value of log $(1/\tau)$, corresponding to a temperature of 4.2°K. In reality the original values of the ordinates of the different curves are different, as is shown for temperatures of 4.2 and 15°K in the figure in[6].

The characteristic feature of the curves shown in Fig. 2, pertaining to temperatures below 25°K, is the presence of maxima. The position of the maxima is shifted towards the side of lower frequencies as the temperature increases. In this connection the value of the maximum decreases, and it disappears completely on the curves pertaining to temperatures of 26 and 34°K. These last curves coincide with each other within the limits of accuracy. It is very unlikely that these maxima were associated with geometrical factors, since the particles of the complex in the sample have a large spread in their dimensions. We further note that the increase of the effective absorption cross section with increasing temperatures begins with increasingly lower frequencies.

## 4. DISCUSSION OF THE RESULTS

The existence of a discontinuity of the specific heat in the complex (NMP)(TCNQ) at 7.2°K undoubtedly indicates the presence of a phase transition, which occurs at this temperature. The nature of the states of the complex above and below the transition point can be ascertained from an analysis of the data shown in Fig. 2. One can easily see that, at 4.2°K the complex exists in a dielectric state. In fact, the abrupt increase of absorption, observed at this temperature at frequencies above 20 $\text{cm}^{-1}$, is obviously related to the presence of a small gap in the spectrum of the electronic excitations. In this connection the origin of the maxima on the curves in Fig. 2 can be explained by the existence of a singularity in the density of electronic states near the gap boundaries. It is well known that such singularities arise in the case of gaps having a collective origin, for example, superconducting and Peierls. Therefore, the position of the maximum can be used for a numerical estimate of the magnitude of the gap.

Thus, we obtain the result that, at 4.2°K the magnitude of the gap amounts to 47 ± 5 $\text{cm}^{-1}$, which corres-

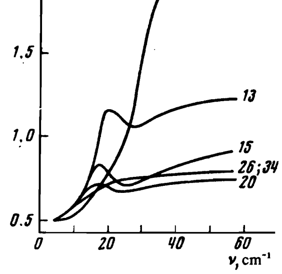

FIG. 2. Frequency dependence of log $(1/\tau)$, reflecting the behavior of the effective cross section for the absorption of radiation by the particles of the complex. At 4 $\text{cm}^{-1}$ all of the curves are tied to the same value of log $(1/\tau)$, corresponding to a temperature of 4.2 °K.

ponds to 68°K. We note that this is an order of magnitude larger than the transition temperature observed according to the discontinuity of the specific heat. The gap in the electronic excitation spectrum of the complex vanishes at temperatures above 20–25°K, and the complex is then found in a metallic state.

From the data of Fig. 2, it is seen that this transition from a dielectric state into a metallic state occurs not so much as a sudden closing of the gap, but rather by means of an increase of the density of states inside the gap and thus by its conversion into a pseudogap. In fact, the position of the maxima varies insignificantly at temperatures of 13, 15, and 20°K: the maxima occur, respectively at the frequencies 20, 17, and 15 $\text{cm}^{-1}$. At the same time their magnitude decreases rapidly, and the maxima are absent on the curves corresponding to temperatures of 26 and 34°K.

The described behavior of the complex is qualitatively in good agreement with the picture of a Peierls transition in quasi-one-dimensional systems, discussed by Lee, Rice and Anderson.[9] In the molecular-field approximation, a gap of the order of 70°K should correspond to a transition temperature $T_p$ of the order of 20°K. It is precisely in this range of temperatures that we observe the onset of the formation of the pseudogap. Allowing for temperature fluctuations, according to Lee, Rice, and Anderson the true phase transition should be equal to $(1/4)T_p$, i.e., 5°K, which is quite close to the observed value of 7.2°K. However, the phase transition observed by us can hardly be treated as a pure Peierls transition, since the fundamental dielectric state of the complex is not diamagnetic.[10]

In conclusion we note that the results discussed in the present work are in good agreement with the results obtained in[5] from an analysis of the electric and magnetic properties of the complex (NMP)(TCNQ). At the same time they cast doubt on the interpretation of the properties of this complex given in[2].

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1) NMP denotes N-methyl-phenazinium and TCNQ denotes tetracyanoquinodimethan.

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