

# Energy gap and metal-dielectric transition in the (NMePh)(TCNQ) complex at low temperatures

F. F. Igoshin, O. N. Eremenko, A. P. Kir'yanov, and I. F. Shchegolev

*Institute of Chemical Physics, USSR Academy of Sciences*

*Moscow Physico-technical Institute*

(Submitted April 15, 1974)

ZhETF Pis. Red. **19**, 644-647 (May 20, 1974)

We have investigated the optical transmission spectra of the high-conductivity complex (NMePh)(TCNQ) in the far-infrared region. A gap that amounts to 65 °K at 4.2 °K and decreases by a factor 2.5 when temperature is raised to 15 °K has been observed in the electronic spectrum of the complex.

The complex (NMePh)(TCNQ)<sup>1</sup> belongs to the class of high-conductivity TCNQ complexes (for a review of their properties see<sup>[1]</sup>) with a half-filled initial conduction band, and with a characteristic internal lattice disorder due to the asymmetry of the NMePh cation. An analysis of its electric and magnetic properties<sup>[2,3]</sup> favors the assumption that at low temperatures it is in the state of a disordered Mott-Hubbard dielectric, which goes over into the state of a one-dimensional disordered metal in the temperature interval between 10 and 30 °K. In the present paper we report a direct experimental observation of the energy gap in the spectrum of the elec-

tronic excitations of this complex at low temperatures.

The complex was compounded of tetracyanoquinodimethane purified by recrystallization and double vacuum sublimation and of phenazine metasulfate purified by double recrystallization. The radiation transmission coefficient was measured in the wavelength interval 0.15–2 mm at 4.2 and 15 °K. The measurements were performed with a single-beam Czerny-Turner type echelette spectrometer. The radiation source was a PRK-4 mercury lamp. The monochromator radiation was modulated at 700 Hz and transmitted through a stainless-steel light pipe to an *n*-InSb detector operating at 4.2 °K. The re-

ceiver sensitivity in the working frequency band, at a 1 Hz bandwidth, was  $\sim 5 \times 10^{-12}$  W. In the absence of the sample, this ensures a signal/noise ratio not less than 500 at a resolution  $0.5 \text{ cm}^{-1}$ . A Michelson spectrometer<sup>[4]</sup> and a procedure described in<sup>[5]</sup> were used to calibrate the monochromator and to check the spectrum frequency.

Contacted 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 2–3%. They were prepared by thorough grinding the two components together in a mortar into which a small amount of liquid nitrogen was poured, followed by pressing of the resultant powder into pellets of 10 mm diameter and of thickness 1 to 2 mm. The dimensions of the complex particles in the sample did not exceed 10 microns. The pellets, in thin brass clips, were placed in the light pipe ahead of the detector. The sample temperature was regulated by displacing the pellets in the light pipe and was measured with a Cu–Cu + 0.12% Fe thermocouple soldered to the clip.

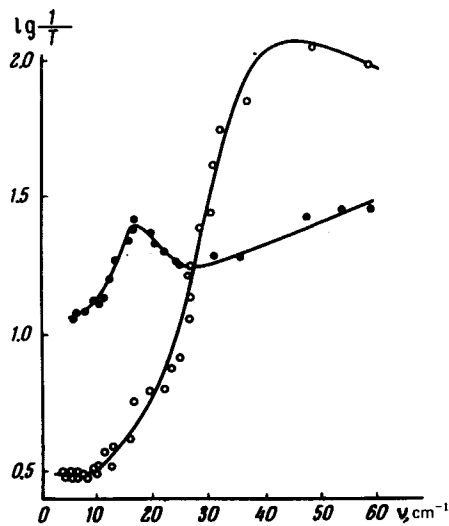
The complex dielectric constant of such composition samples has a complicated dependence on the properties of both components. For a qualitative analysis of the results, however, one can note the following. The dimensions of the particles of the complex as well as the distances between them are small in comparison with the wavelength, so that diffuse scattering of the radiation in the sample is small in comparison with the specular reflection from its boundaries. Since, furthermore, there is practically no intrinsic absorption in the paraffin, the transmission coefficient  $T$  can be represented with sufficient accuracy in the form

$$T = (1 - R)^2 \exp(-n\sigma d),$$

where  $R$  is the coefficient of reflection from the surface,  $\sigma$  is the effective cross section of the absorption of the radiation by the particles of the complex,  $n$  is their concentration, and  $d$  is the sample thickness.

Further, in view of the low concentration of the complex, the reflection coefficient  $R$  is determined mainly by the properties of the paraffin and should not change greatly with changing frequency. The frequency dependence of  $\log(1/T)$  should duplicate, at least in principal outline, the frequency dependence of the effective absorption cross section<sup>2)</sup>.

The figure shows the frequency dependences of  $\log(1/T)$ , measured for one of the samples at 4.2 and 15°K. The abrupt increase of absorption at frequencies above  $20 \text{ cm}^{-1}$  at 4.2°K proves, in our opinion, the presence of a small gap in the spectrum of the electronic excitations of the complex. The maximum of the absorption at  $45 \text{ cm}^{-1}$  is mostly probably due to a singularity in the density of states near the gap boundaries, and the position of the maximum can be used for



Frequency dependence of  $\log(1/T)$ : ○—4.2°K, ●—15°K.

a numerical estimate of its magnitude. At 15°K, the position of the maximum shifts towards lower frequencies, thus indicating a decrease of the gap by an approximate factor 2.5. At high frequencies the two curves exhibit a tendency to merge, which is natural, since a noticeable restructuring of the energy spectrum should occur only near the Fermi level.

For the superconducting and Peierls transitions, the transition temperature  $T_c$  is smaller by a factor 3.5 than the size of the gap at 0°K. If we use the same ratio to estimate the transition temperature in our case, we obtain  $T_c \approx 20$ °K. We note that this value of  $T_c$  does not agree well with the conclusion of<sup>[6]</sup>.

We are deeply grateful to L.N. Bulaevskii and A.I. Larkin for useful discussions.

<sup>1)</sup>NMePh–N-methylphenazinium, TCNQ–tetracyanoquinodimethane.

<sup>2)</sup>Estimates using the values of the conductivity of the complex at a frequency  $1.25 \text{ cm}^{-1}$  ( $\lambda = 8 \text{ mm}$ ) show that in the working range of frequencies and temperatures the particle dimensions are apparently much less than the depth of the skin layer. Under these conditions, the absorption cross section is in turn proportional to the conductivity of the complex.

<sup>1</sup>I. F. Shchegolev, Phys. stat. solidi (a) 12, 9 (1972).

<sup>2</sup>L. N. Bulaevskii, A. V. Zvarykina, Yu. S. Karimov, R. B. Lyubovskii, and I. F. Shchegolev, Zh. Eksp. Teor. Fiz. 62, 725 (1972) [Sov. Phys.-JETP 35, 384 (1972)].

<sup>3</sup>L. N. Bulaevskii, R. B. Lyubovskii, and I. F. Shchegolev, ZhETF Pis. Red. 16, 42 (1972) [JETP Lett. 16, 29 (1972)].

<sup>4</sup>F. F. Igoshin, A. P. Kir'yanov, V. V. Mozhaev, M. A. Tulaikova, A. A. Sheronov, Prib. Tekh. Éksp. No. 1, 159 (1973).

<sup>5</sup>A. N. Gergobiani, F. F. Igoshin, A. P. Kir'yanov, V. V. Mozhaev, M. A. Tulaikova, and A. A. Sheronov, Kratkie soobshcheniya po fizike (FIAN SSSR), No. 3, 51 (1972).

<sup>6</sup>A. J. Epstein, S. Etemad, A. F. Garito, and A. J. Heeger, Phys. Rev. B5, 952 (1972).