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LOCALIZED CHARACTER OF ELECTRONIC STATES IN THE HIGHLY CONDUCTING COMPLEX TCNQ WITH DITOLUOLCHROMIUM AT LOW TEMPERATURES

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1. Complex compounds of tetracyanoquinodimethane (TCNQ) with typical composition R^+TCNQ^- (simple salts) and $R^+(TCNQ)_2^-$ (complex salt), where R is the molecule of the second component of the complex, are of interest as objects possessing a noticeable electric conductivity of the quasi-one-dimensional type (a survey of their properties is given in [1]). A general feature of the crystal structure of these compounds is the presence of weakly coupled stacks of TCNQ molecules, along which electrons supplied by the second component of the complex can move more or less freely.

From the point of view of formal arguments of the band theory, at least some of the TCNQ complexes should be metals, but actually the temperature dependence of their conductivity, measured on single crystals, is of the activation type in the greater part of the temperature band. One of the causes of such a behavior might be the transition from the metallic (or almost metallic) state to a state of a Mott insulator with electrons localized on the sites. The presently known x-ray data show that in well-conducting complex TCNQ salts all the TCNQ molecules in the stack have at room temperature a uniform molecular geometry, intermediate between $TCNQ^0$ and $TCNQ^-$ [2], which is evidence of delocalization of the outer electron. We do not know, however, whether such a delocalization is maintained at low temperatures.

This question can be answered in some cases by measuring the paramagnetic shifts of the proton-resonance lines of the TCNQ molecules in well-conducting complex salts. We report here the results of an NMR study of a complex of TCNQ with ditoluenchromium (DTC) with composition $(DTC)(TCNQ)_2$. These results indicate that at low temperatures the external electron in this well-conducting complex salt is localized at every other TCNQ molecule.

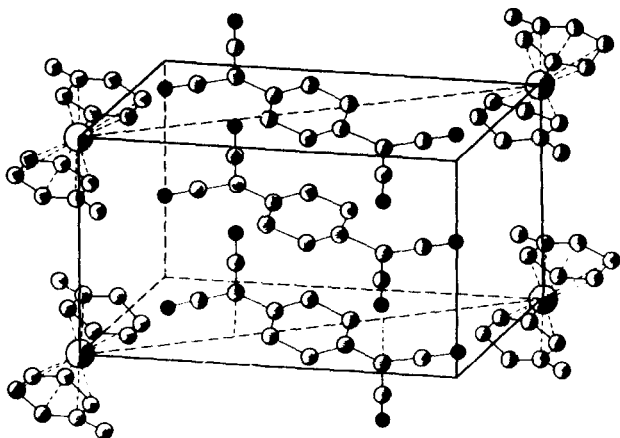


Fig. 1. Structure of unit cell of the $(DTC)(TCNQ)_2$ complex. We have omitted from the figure, for clarity, certain DTC molecules located at each vertex of the parallelepiped.

2. With respect to its physical properties and crystal structure, the complex $(DTC)(TCNQ)_2$ belongs to the class of well-conducting TCNQ complexes [3]. The structure of the unit cell of the complex is shown schematically in Fig. 1 [4]. Although from the formal chemical point of view the complex contains one neutral TCNQ molecule and one anion-radical $TCNQ^-$, all the TCNQ molecules in the stack are at equal distances, 3.29 Å, from one another and have the same relative placement. The unit cell contains two crystallographically-nonequivalent TCNQ molecules, which differ in their cation surroundings, and therefore from the point of view of the band theory the stacks of TCNQ molecules should be metallic with a half-filled conduction band. It was shown in [3] that in this complex there exist two practically independent spin systems, one of which is connected with the DTC cation-radicals, and the other with the TCNQ anion-radicals.

3. Figure 2 shows plots of the derivatives of the NMR lines from the TCNQ protons, obtained at helium temperatures. The presence of an unpaired spin at the DTC molecules leads to a strong paramagnetic shift of their proton lines, which lie at the lowest temperatures beyond the limits of the field interval shown in the figure. This is precisely why this complex is a unique object that enables us to trace the behavior of the electrons of the TCNQ chains with the aid of nuclear magnetic resonance.

All four protons of the TCNQ molecule are equivalent. As seen from the figure, however, the spectrum is a poorly resolved doublet, and the distance between its components increases with decreasing temperature. The position of the narrower line of the doublet coincides, within the limits of measurement errors (± 2 Oe), with the position of the proton line in the diamagnetic compound. The other line is shifted towards the paramagnetic side and is strongly broadened.

Since the lines are not fully resolved even at the lowest temperature, their relative intensities cannot be accurately determined, but the ratio 1:1 seems most likely. In this case the shift Δ of the center of gravity of the displaced line will be equal to double the shift of the center of gravity of the entire spectrum and can be easily measured. It is seen in Fig. 3 that when the temperature is decreased Δ increases approximately like $1/T$.

4. The non-equivalence of the TCNQ molecules in the investigated complex complicates the interpretation of the results somewhat. In the presence of large covalence in the coupling between the DTC and TCNQ, the spin density can be partly transferred from the cation to the nearest anion, and it may turn out that the presence of two lines from the protons of the TCNQ molecules may be entirely due to this circumstance only. This covalent increment, however, will be realized principally just by the electron that ensures the high conductivity

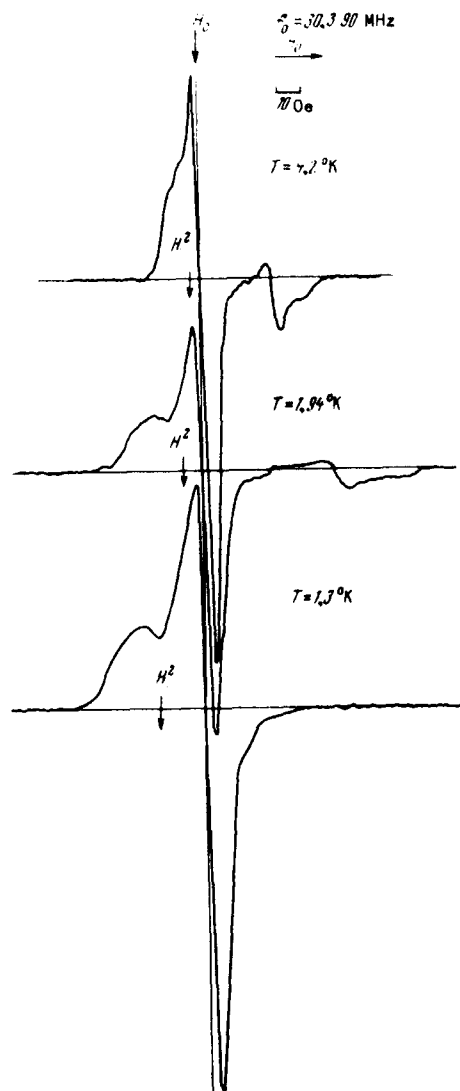


Fig. 2. Plots of derivatives of NMR lines from the TCNQ protons, obtained at helium temperatures.

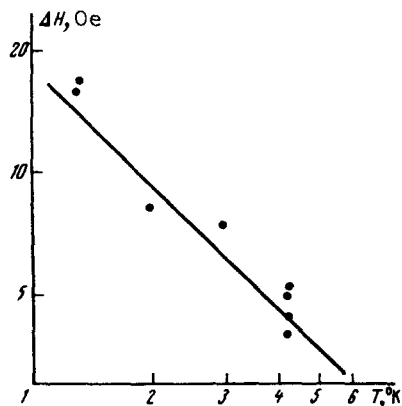


Fig. 3. Temperature dependence of the NMR line shift.

along the chains, since the contribution from the internal electrons of the TCNQ should be much weaker, owing to their large binding energy. The transferred spin density would therefore be distributed over the chain, mainly in accordance with the character of the distribution of the density of the external electron, i.e., uniformly, if the electron is delocalized, and non-uniformly in the opposite case, leading only to a slight modification of the effective field.

On the other hand, if it is assumed that the observed line splitting is nevertheless somewhat connected with the transfer of the spin density of the cation via the internal electrons of the TCNQ molecules, whereas the external electron is delocalized, then one should expect an overall shift of both lines by an amount which is in any case not smaller than the magnitude of the splitting, something not observed in fact.

We can thus conclude that at helium temperatures the extra electrons of the linear conducting chains in the (DTC)(TCNQ)₂ complex are localized. If these electrons were delocalized at room temperature, as in the other well-conducting complex TCNQ salts, then we could conclude that when the temperature is lowered there occurs in the investigated complex something similar to a Mott transition. Unfortunately, in view of the low accuracy with which the bond lengths in (DTC)(TCNQ)₂ have been determined at room temperature ($\pm 0.03 \text{ \AA}$) [4], this statement cannot be regarded as final. More accurate x-ray measurements are of great interest in this connection.

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STABILIZATION OF RING-LASER FREQUENCY

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1. We report the results of an experiment on the development of an optical ($\lambda = 3.39 \mu$) frequency standard with a relative frequency stability $\Delta\nu/\nu = 5 \times 10^{-14}$. The role of the frequency discriminator is assumed by the resonances of the power in the radiation of a ring laser with a nonlinearly-absorbing methane cell inside the resonator [1, 2].

At present, the most effective methods of frequency stabilization in the optical band are based on the use of power resonances of lasers that fix the central frequency of atomic or molecular transitions. Thus, stabilization of