

Low-temperature phase transition in the $\text{Qn}(\text{TCNQ})_2$ complex

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(Submitted July 29, 1974)

ZhETF Pis. Red. 20, No. 6, 404-407 (September 20, 1974)

Results are presented of the measurements of the specific heat of the high-conductivity organic complex $\text{Qn}(\text{TCNQ})_2$ in the temperature interval 11-17.5°K. A jump in the specific heat is observed at 14°K and is connected with the metal-dielectric phase transition in the quasi-one-dimensional electronic system of the complex. The magnitude of the jump is close in order of magnitude to the electronic part of the specific heat of the complex at the transition point.

In single crystals of the high-conductivity organic complex $\text{Qn}(\text{TCNQ})_2$, the TCNQ anions, which carry unpaired electrons, are arranged as regular parallel chains that are separated in space by chains of the quinoline (Qn) cations. From the point of view of the band theory, this complex is a quasi-one-dimensional metal, one-quarter of whose initial conduction band is filled.

An analysis of various experimental data^[1,2] shows that at sufficiently high temperatures ($T > 20^\circ\text{K}$) the electronic system of this complex is indeed metallic. At the present time, however, there is no agreement as to the state of this system at lower temperatures. Thus, the authors of^[3,4] conclude on the basis of measurements of the specific heat in the interval from 1.5 to 4.5°K that the conducting chains in $\text{Qn}(\text{TCNQ})_2$ remain metallic down to absolute zero. On the other hand, an analysis of the electric and magnetic properties of this complex, carried out in^[1], favors the assumption that its electronic system goes over from the metallic phase into a disordered phase of a Mott-Hubbard dielectric in the region 10-20°K.

To determine whether a phase transition takes place in $\text{Qn}(\text{TCNQ})_2$, we measured its specific heat in the temperature interval 1.5-17.5°K. The measurements were performed by the usual adiabatic method with the setup described in^[5]. The temperature dependence of the total specific heat of the calorimeter with the sample in the interval 11-17.5°K is shown in logarithmic coordinates in Fig. 1. In these coordinates, the temperature dependence of the specific heat in the indicated region of

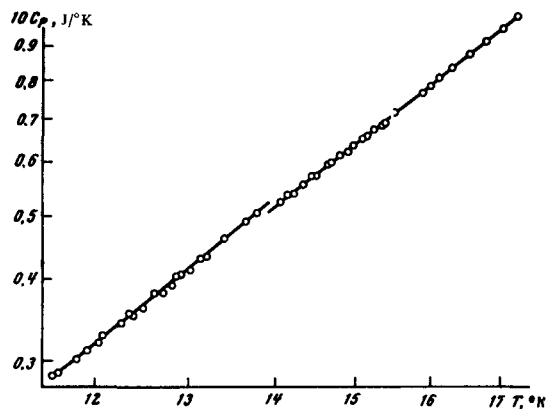


FIG. 1. Temperature dependence of the total specific heat of the calorimeter with the sample in the interval 11-17.5°K.

temperatures is well approximated by two straight lines. The slopes of lines correspond to a specific heat proportional to $T^{3.26}$ in the region $T < 14^\circ\text{K}$ and to $T^{3.14}$ at $T > 14^\circ\text{K}$. The rms deviation of the experimental points from the smoothing lines does not exceed 0.5% for the low-temperature section and 0.2% for the high-temperature section. At $T = 14^\circ\text{K}$, a jump is observed in the specific heat. The magnitude of the jump is approximately 3% of the total specific heat and greatly exceeds the rms random error.

We are using the total measured specific heat to avoid the additional error that results from subtracting the contribution of the anticalorimeter. The measurements show that this contribution does not exceed 20% in the interval 11-17.5°K, and its temperature dependence is smooth.

For a more detailed investigation of the character of the jump, we subtracted from the total specific heat the regular part corresponding to extrapolation of the high-temperature section to the entire temperature interval. The results are shown in Fig. 2. We see that the jump greatly exceeds the average random scatter of the points. The course of the specific heat agrees in this case with its usual behavior in second-order phase transitions.

The observed jump of the specific heat is apparently connected with a phase transition in only the electronic system of the complex. In fact, in structural transitions one can expect the jump to be of the same order as the specific heat of the lattice at the transition point. The observed jump, however, is smaller than the latter by a factor 20-25.

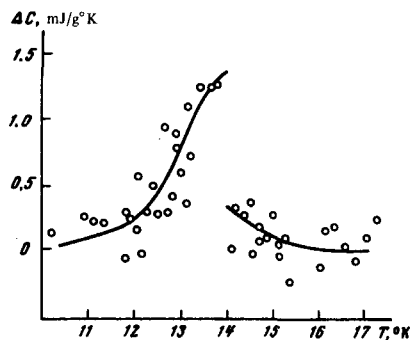


FIG. 2. Jump of electronic specific heat of the complex $\text{Qn}(\text{TCNQ})_2$ at 14°K.

On the other hand, the magnitude of the jump, $\Delta C = 1.3 \text{ mJ/g}^\circ\text{K}$, is close to the value of the electronic part of the specific heat of the complex at the transition point. Indeed, if the electronic system of the complex is in the metallic state at $T > 14^\circ\text{K}$, then its specific heat is $C_e = (\pi^2/3) g(\epsilon_F) k^2 T$, where $g(\epsilon_F)$ is the density of states at the Fermi level and k is Boltzmann's constant. The value of C_e at 14°K can be easily estimated by using the value of $g(\epsilon_F)$ calculated from the Pauli paramagnetic susceptibility $\chi_P = \mu_B^2 g(\epsilon_F)$, and the value $\chi_P = 0.65 \times 10^{-6} \text{ cm}^3/\text{g}$ corresponding to the minimum on the $\chi(T)$ curve.^[6] This yields $C_e(14^\circ\text{K}) = 0.67 \text{ mJ/g}^\circ\text{K}$.

The near equality of $C_e(14^\circ\text{K})$ and ΔC indicates once more that at $T \gtrsim 14^\circ\text{K}$ the electronic system of $\text{Qn}(\text{TCNQ})_2$ goes over into the metallic state. From the results of measurements of the specific heat alone it is difficult to assess the nature of the observed transition. However, the transition could hardly be of a pure

Peierls type, for in the case of the Peierls transition the substance should become diamagnetic at $T < T_p$, whereas the complex $\text{Qn}(\text{TCNQ})_2$ is a disordered one-dimensional antiferromagnet at low temperatures.^[6]

We are grateful to M.L. Khidekel' and É.B. Yagubskii for synthesis of the complex and to L.N. Bulaevskii for useful discussions.

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