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Investigation of phase transition in Qn(TCNQ)$_2$ by the nuclear magnetic resonance method

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The temperature dependences of the paramagnetic shifts and of the line widths of proton resonance in Qn(TCNQ)$_2$ are investigated in the temperature interval 1.6–78 K in a magnetic field 47.4 kOe. The observed nonmonotonic dependence of the paramagnetic shift on the temperature indicates that a restructuring due to a phase transition takes place in the electron system of the complex near 10 K.

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1. INTRODUCTION

By now there is practically no doubt that at temperatures above 20–30 K the quasi-one-dimensional electron system of the complex1) Qn(TCNQ)$_2$ is in a metallic state that becomes possibly stabilized because of the presence of an internal structural disorder due to the random packing of the asymmetrical cations. In particular, the temperature dependence of the conductivity and of the dielectric constant of this complex can be described quite satisfactorily within the framework of the single-electron theory that takes into account the joint influence of the disorder and of the phonons on the kinetics of a one-dimensional metal.[1]

At the same time, an analysis of the unusual low-temperature magnetic properties of the complex[2,3] has led to the conclusion that it can undergo a phase transition, in the region 10–20 K, from the state of a one-dimensional disordered metal into the state of a one-dimensional disordered dielectric of the Mott type. The subsequent study of the temperature dependence of the heat capacity of the complex[4] has revealed at 14 K a heat-capacity jump whose existence and magnitude favor the foregoing conclusion.

To obtain more detailed information on the character of the low-temperature phase transition in Qn(TCNQ)$_2$, we have investigated the behavior of the proton magnetic resonance lines in this compound in the temperature interval 1.6–78 K. In view of the smallness of the electron-proton hyperfine interaction constant in the TCNQ molecule and the smallness of the paramagnetic susceptibility of the complex, the measurements were made in fields of the order of 50 kOe to obtain measurable paramagnetic line shifts.

2. MEASUREMENT PROCEDURE

We used the simplest NMR spectrometer variant. The main magnetic field, 47376.75 Oe, was produced with a superconducting solenoid operating in the short-circuit regime. The sample was a pellet of 5 mm diameter and 5 mm length. The inhomogeneity of the field in the volume of the sample did not exceed 0.05 Oe, and the relative instability did not exceed 10^{-8} per hour.

The proton resonance signal was registered by Rollin's method with a pickup of the type described in[5]. The high-frequency source was a generator of type GZ-20, the filament of the generator tube being fed with stabilized direct current. The frequency was measured with a digital Ch3-38 frequency meter. After heating for 1.5–2 hours, the instability of the generator frequency during the time required to record the lines (several minutes) was $(2-3)\times10^{-6}$. The pickup with the sample were placed in a separate cryostat inside the solenoid, and its temperature could be varied either with a heater wound on an external copper screen, or by pumping off helium vapor. Temperatures higher than 4.2 K were measured with a copper–gold thermocouple. The temperature in this range was maintained constant within ±0.5 K.

Passage through the resonance line was with the aid of a small superconducting coil placed inside the main solenoid. The voltage, proportional to the current in the coil, was fed to the X terminals of an x-y recorder, and the resonance signal was applied to the Y terminals. The calibration of the coil, as well as the measurement of the field of the main solenoid, were based on the proton-resonance signal of rubber at room temperature.

3. MEASUREMENT RESULTS

In the entire investigated temperature interval, we have observed a single resonance line, the shape of which is fairly well approximated by a Gaussian curve. Figure 1 shows the temperature dependence of the shift δH of the center of the resonance line from the position typical of protons in a diamagnetic compound. For those temperatures at which more than five measurements were made, the plot shows the average values of the shifts, and the rms random error is indicated.

As seen from the insert of Fig. 1, the paramagnetic shift is proportional to the susceptibility of the complex down to a temperature 8 K, within the limits of the measurement accuracy. We thus obtain one more proof that the low-temperature increase of the susceptibility of the complex is determined by its intrinsic electron system and is not due to the presence of paramagnetic impurities. We can determine next from these data the hyperfine interaction constant a, using the formula

$$\delta H = a\chi H\rho/\hbar\gamma N,$$

where γ is the nuclear gyromagnetic ratio, N is Avogadro's number, χ is the molar susceptibility, and $\rho \approx \frac{1}{2}$ is the spin density at the TCNQ molecule. We obtain thus $a = 2$ Oe, in fair agreement with the value 1.6 Oe known from the analysis of the hyperfine structure of the ESR spectrum.[6] Below 8 K, the paramagnetic shift begins to decrease rapidly, reaching a minimum at 2.5 K, after which it increases somewhat.

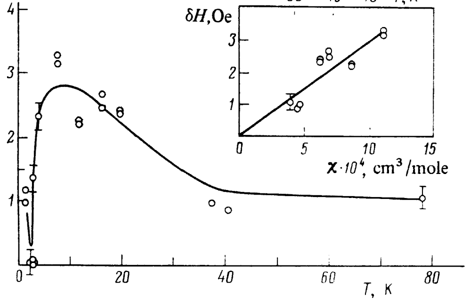

FIG. 1. Paramagnetic shift of proton line vs temperature. The insert shows the paramagnetic shift as a function of the susceptibility, whose value was taken from[2].

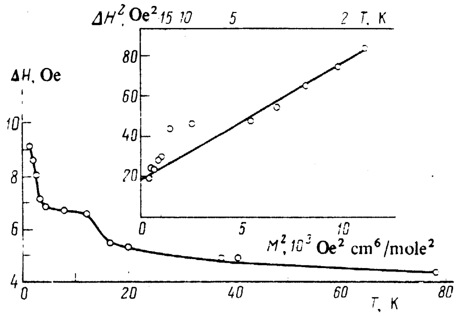

FIG. 2. Temperature dependence of the proton line. The insert shows the square of the width as a function of the square of the electronic magnetic moment.

Figure 2 shows the temperature dependence of the resonance-curve width ΔH obtained by measuring the distance between the peaks of the derivative. The measurement accuracy of this quantity is ± 5%. Generally speaking, a quantity more amenable to interpretation is not the line width but its second moment M_2. A direct experimental determination of this moment, however, being a rather laborious operation, is not justified in most cases, since it is subject to a considerable uncertainty due to the leeway in the estimate of the contribution of the line wings. Inasmuch as in our case the resonance curves hardly change shape with changing temperature, the second moment can be expressed with good accuracy in terms of the proportional quantity ΔH^2. In particular, $M_2 = \Delta H^2/4$ for a Gaussian line.

In the case of polycrystalline samples one can distinguish between four additive contributions to the second moment:

1) The contribution due to thermal-relaxation processes, which is always negligibly small for solids at low temperature.

2) The contribution due to nuclear-nuclear interactions. This contribution is independent of the magnetic fields and is also independent of temperature at low temperatures.

3) The contribution due to the anisotropic part of the hyperfine interaction; it is proportional to the square of the electronic magnetization.

4) The contribution due to the isotropic part of the hyperfine interaction; it does not vanish only if this interaction is inhomogeneous. This contribution should be

proportional to the square of the paramagnetic shift δH.

To separate the roles of the different contributions to the second moment, the insert of Fig. 2 shows the dependence of the squared line width ΔH^2 on the squared electronic magnetic moment M^2. For temperatures between 10 and 78 K the electronic magnetic moment is taken to be $M = \chi H$. For lower temperatures we use Bulaevskiĭ's formula[2]

$$M=g\mu_B NAT^{1-\alpha}f(g\mu_B H/kT),$$

which, no matter what we think of its derivation, describes adequately the experimental results in this region.

It is seen from the figure that in the temperature region where the paramagnetic shift reaches a maximum, the second moment noticeably exceeds the values expected from the sum of contributions 2) and 3). This is one more proof that the shifts observed by us are real, and seems to indicate that they are noticeably inhomogeneous.

4. DISCUSSION

The first question that must be discussed in connection with the reported results is why a single proton-resonance line is observed at all temperatures. The molecule of the complex contains 8 protons of quinoline and 8 protons of TCNQ. In a polycrystalline sample, the shift of the line center is due only to the Fermi contact interaction, and if the spin density at the quinoline molecules were zero, we would have a doublet with one component located in the position of the undisplaced proton line. At temperatures close to 10 °K the line has a width 6-7 Oe, and the shift of its center amounts to ~3 Oe. Under these conditions it is impossible not to note the doublet character of the line.

We have performed special experiments in which the lines were recorded at gradually decreasing levels of the high-frequency power. They have shown that the absence of an undisplaced line cannot be attributed to its saturation. It must therefore be assumed that the spin density at the quinoline molecule is different from zero, and it is this circumstance which leads to paramagnetic quinoline proton-line shifts that are close in magnitude to the TCNQ proton-line shifts. We note in this connection that the existence of a single proton line in $Qn(TCNQ)_2$ correlates with the fact that this compound has only one spin-lattice relaxation time.[7]

Since the hyperfine interaction constant a_{Qn} in the quinoline radical is unknown, we cannot estimate the spin density that should exist at the quinoline molecule. We indicate only that it can be small: if, for example, $a_{Qn} = 2a_{TCNQ}$, then 20% of spin density at the quinoline molecule is sufficient to produce the same paramagnetic shift as in the TCNQ molecule. We note also that owing to the presence of electrons of the filled molecular orbitals, the spin density, of course, does not coincide with the value of the electron density.

We propose that the nonmonotonic temperature dependence of the paramagnetic shift, shown in Fig. 1, is due to a restructuring of the electronic states in the $Qn(TCNQ)_2$ complex at temperatures below 10 K, which causes the hyperfine-interaction constants to decrease greatly. This restructuring is due to a phase transition in the electron system of the complex. It is difficult at present to explain why this restructuring takes place at temperatures below the temperatures at which the heat capacity has a discontinuity. This may be due both to the influence of the strong magnetic field and to the difference between the methods used to observe the phase transition.

In conclusion, we thank L. N. Bulaevskiĭ and L. P. Gor'kov for a discussion of the work and for valuable remarks.

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