SOVIET PHYSICS JETP VOLUME 35, NUMBER 2 AUGUST, 1972

Magnetic Properties of Linear Conducting Chains

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Submitted August 22, 1971

Zh. Eksp. Teor Fiz. **62**, 725–736 (February, 1972)

The temperature dependences of the susceptibility of three highly conducting tetracyanoquinodimethan (TCNQ) complexes with the compositions quinoline$^+$(TCNQ)$_2^-$, acridine$^+$(TCNQ)$_2^-$ and phenazine$^+$(TCNQ)$^-$ have been studied at temperatures between 0.1 and 400°K. Magnetization curves in fields up to 70 kOe have been measured between 0.1 and 4°K. It is shown that the low-temperature increase in the susceptibility, characteristic of highly conducting TCNQ complexes, is not connected with the presence of paramagnetic impurities in the samples, but reflects properties of the complexes themselves. An analysis of the experimental results shows that the distinctive low-temperature magnetic properties of the complexes investigated are a manifestation of a singularity in the density of states of disordered quasi-one-dimensional systems, the quasi-one-dimensional electron system being in a "Mott" insulator state with localized electrons at $T=0$.

1. INTRODUCTION

THE theoretical study of the physical properties of a one-dimensional conducting chain[1,2] shows that the question of precisely which states can actually be realized in a one-dimensional case, with the electron-electron and electron-phonon interactions taken into account, is non-trivial even in the case of zero temperature and is far from being completely clarified at the present time. This makes it of interest to investigate experimentally the different properties of substances in which the one-dimensionality of the electron system is established by features of their crystal structure and which at the same time possess a considerable electrical conductivity.

Examples of such substances are complex salts of tetracyanoquinodimethan (TCNQ) with typical compositions R$^+$(TCNQ)$^-$ (simple salts) and R$^+$(TCNQ)$_2^-$ (complex salts), where R is the molecule of the cation, different in different complexes. A characteristic feature of the crystal structure of these compounds is the presence of stacks of TCNQ molecules,[3,4] almost isolated from each other, along which the conduction occurs preferentially.[5]

Formally, each molecule of the complex always contains one unpaired electron, and this makes it paramagnetic. In the simple salts, there is an unpaired electron in each unit of the linear conducting chain composed of the TCNQ molecules. In the complex salts, there is one unpaired electron to each two units of the linear conducting chain. Here, it is important to note that, in the highly conducting complex salts, all the TCNQ molecules in the chain are completely equivalent[4] and it is not possible to establish in precisely which units an unpaired electron is to be found.

Between the electrical and magnetic properties of the TCNQ complexes there exists a close correlation, noted in the very first papers on this subject,[6,7] which is clear evidence that both types of property are determined by the same group of electrons. It may be hoped, therefore, that the study of the magnetic properties of these complexes, especially at low temperatures, will make it possible to obtain information on the states of their electron system.

In the present work, we have measured the temperature dependence of the susceptibility of three highly conducting complexes of tetracyanoquinodimethan, of compositions: I – quinoline$^+$(TCNQ)$_2^-$, II – acridine$^+$(TCNQ)$_2^-$, and III – phenazine$^+$(TCNQ)$^-$ in the temperature range 0.1–400°K, and have plotted the magnetization curves in fields up to 70 kOe in the temperature range 0.1–4°K. Special attention was given to proving that the increase in susceptibility at the lowest temperatures is not connected with the presence of paramagnetic impurities in the samples, but reflects the properties of the samples themselves. An analysis of the experimental results shows that the distinctive low-temperature magnetic properties of the complexes investigated are a manifestation of a singularity in the density of states of one-dimensional disordered systems.

2. RESULTS OF THE MEASUREMENTS

1. The magnetic susceptibility χ of the complexes in the temperature range 1.6–400°K was measured on a magnetic balance[8] using Faraday's method. The paramagnetic contribution χ_{para} to the susceptibility was determined as the difference $\chi - \chi_{\text{dia}}$, the diamagnetic contribution χ_{dia} of the substrate being calculated from Pascal's rules. The values thus obtained for the paramagnetic susceptibility are presented as a function of temperature in Fig. 1.

In the high-temperature region (above ~30°K for complexes I and II and above ~80°K for complex III), χ_{para} changes little with temperature. For complexes I and II, there is a weak maximum here, in the region of 300 and 250°K respectively. For complex III, this maximum lies, apparently, at a temperature somewhat above 400°K. In the low-temperature region, the susceptibility of all three complexes begins to increase rather rapidly on lowering of the temperature. It has already been observed by Kepler[7] that this low-temperature increase in susceptibility (which, we note, is characteristic of all the highly conducting TCNQ complexes known to us) is less likely to be connected with the presence of paramagnetic impurities in the samples than to be a property of the complexes themselves. We shall now describe the results which establish this as a certain fact.

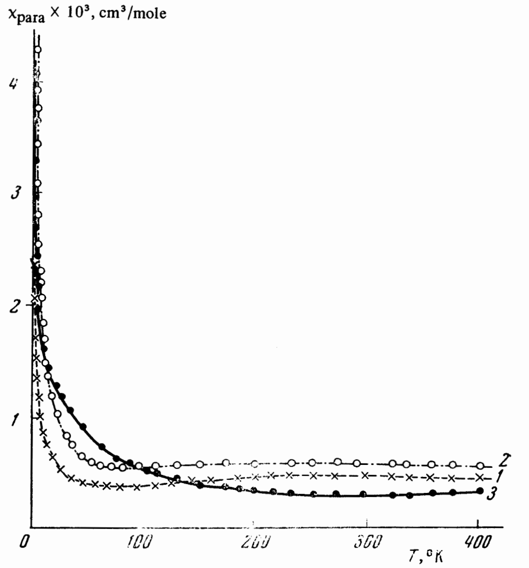

FIG. 1. Temperature dependence of the paramagnetic susceptibility of complexes I–III in the interval 1.7–400°K: 1) complex I, 2) complex II, 3) complex III.

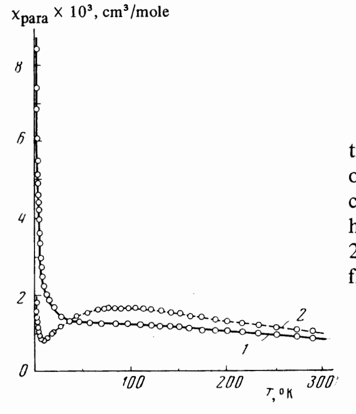

FIG. 2. Paramagnetic susceptibility of the two modifications of the complex (diethylthiazolinocarbocyanin)$^+$(TCNQ)$_2^-$: 1) the highly conducting modification, 2) the poorly conducting modification.

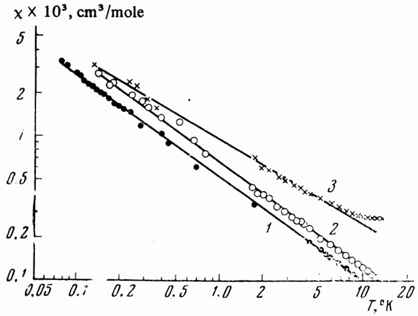

FIG. 3. Temperature dependence of the paramagnetic susceptibility of the complexes I–III in the interval 0.1–10°K: 1) complex I, 2) complex II, 3) complex III.

It has been found [9] that some TCNQ complexes can exist in several crystalline modifications. This is so, in particular, for the complex of composition diethylthiazolinocarbocyanine$^+$(TCNQ)$_2^-$, which exists in two crystalline modifications, differing from each other in the external appearance of the crystallites, in their Debye crystallograms, and in their physical properties. In particular, one of the modifications is highly conducting, while the other belongs to the poorly conducting TCNQ complexes. It is important to note that one modification can be obtained from the other, merely by changing the conditions of crystallization.[9]

In Fig. 2, in which the behavior of the paramagnetic susceptibility of the two modifications of this complex is shown, Curve 1 refers to the highly conducting modification, and curve 2 to the poor conductor. If the increase in susceptibility at low temperatures were connected with the presence of paramagnetic impurities, in obtaining the highly conducting from the poorly conducting modification we should have also obtained, as a consequence, an insignificant increase in susceptibility. However, a considerable increase in χ_{para}, characteristic for the highly conducting TCNQ complexes, can be reproduced with high accuracy in this operation (at 1.7°K, χ_1 is approximately five times greater than χ_2). It follows from this that the low-temperature increase in susceptibility, or at least the largest part of it, is an intrinsic property of the highly conducting TCNQ complexes, and the study of magnetic properties at low and extremely low temperatures can give information about the state of the one-dimensional electron system as $T \to 0$.

2. The magnetic properties of the complexes in the region of extremely low temperatures were studied by a ballistic method. The sample was attached by vacuum cement to one end of a cold-conductor, coiled out of several hundred enameled fine copper wires of diameter 0.04 mm. The other end of the cold-conductor was attached mechanically to copper wires imbedded in a pill of iron ammonium alum of diameter 20 mm and length 70 mm. To measure the temperature, a monocrystal of cerium magnesium nitrate, mounted inside the cold-conductor at a distance of 50 mm from the sample, was used. The magnetic fields for the adiabatic demagnetization of the pill and for measuring the magnetic moment of the samples were produced by two superconducting solenoids. A pair of measuring coils were connected in opposition and each contained 5000 turns. To calibrate the ballistic kicks, values of the susceptibility at 1.7°K, obtained in measurements on the magnetic balance, were used.

The temperature dependence of the paramagnetic susceptibility of the investigated complexes in the temperature range 0.1–10°K is shown in logarithmic coordinates in Fig. 3. It is clear that in this region of temperature, the behavior of the susceptibility does not follow the Curie law, and is well described by the dependence $\chi \propto T^{-\alpha}$, where $\alpha = 0.73$, 0.74, and 0.58 for complexes I, II, and III respectively. It should be noted that such a fractional-power temperature dependence of the low-temperature susceptibility is, apparently, characteristic of all the highly conducting TCNQ complexes. In particular, we have studied the behavior of the magnetic susceptibility of more than ten complexes of this type in the temperature range 1.6–30°K, and for all of these, at temperatures $T \leq 10$–15°K, $\chi_{para} \propto T^{-\alpha}$, with α in the range from 0.55 to 0.75.

A characteristic feature of the magnetization curves of the complexes investigated is the fact that at the lowest temperatures ~0.1°K and in fields up to 70 kOe, the magnetic moment still does not reach saturation. From Fig. 4, which presents in logarithmic coordinates the dependence of the moment M_{para} on the field H for the

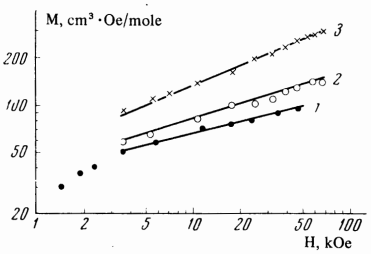

FIG. 4. Dependence of the magnetic moment of complexes I–III on the field in strong fields at extremely low temperatures: 1) complex I at T = 0.115°K, 2) complex II at T = 0.144°K, 3) complex III at T = 0.118°K

complexes I (T = 0.115°K), II (T = 0.144°K) and III (T = 0.118°K), it can be seen that in strong fields (H > 5 kOe), $M \propto H^{\gamma}$, where γ is equal to 0.25, 0.29, and 0.42 respectively.

3. INTERPRETATION OF THE RESULTS

A. The High-temperature Region

The behavior of the magnetic susceptibility in the region where it depends weakly on temperature can be explained in practice with equal success both by the properties of a one-dimensional "Mott" insulator, and by the properties of a one-dimensional metal.

1. A "Mott" insulator is realized when the resonance integral for an electron transition from one molecule to another is not large enough and the electrons are localized on the molecules because of the stronger Coulomb repulsion. For T → 0, we then have a regular arrangement of electrons along the chain (one per TCNQ molecule for complex III, and alternation of molecules with an electron and without an electron for complexes I and II). In this case, the magnetic structure of the unpaired TCNQ electrons is described by a one-dimensional Heisenberg spin Hamiltonian with antiferromagnetic interaction:

$$\mathscr{H} = \sum_m [2J_m S_m S_{m+1} - g\mu_B H S_m^z], \qquad (1)$$

with $J_m = J_0$ for a regular chain. According to the calculations of Bonner and Fisher,[10] for the Hamiltonian (1) with $J_m = J_0$, the susceptibility tends to a constant value as the temperature is lowered, passing through a maximum, whose magnitude is connected with its position by the relation $\eta = (\chi kT)_{\max}/g^2\mu_B^2 N = 0.095$. This behavior is close to that observed experimentally; for the complexes I and II, we obtain $\eta = 0.10 \pm 0.01$, while for complex III, the quantity $\eta \gtrsim 0.1$.

2. To describe the properties of the chain in the metallic model of noninteracting electrons, we can use the tight-binding approximation, since because of the comparatively large spacings between the units (3.2–3.4 Å), the overlap of the electron functions of non-neighboring molecules will be negligibly small. In this case, the magnitude of the magnetic susceptibility can be calculated from the formula

$$\frac{\chi}{g^2\mu_B^2 N} = \frac{1}{2\pi kT}\int_{-\pi/2}^{\pi/2} dt\, \mathrm{ch}^{-2}\frac{\beta(z-\sin t)}{2kT}, \qquad (2)$$

where β is the half-width of the band and z is determined by the condition

$$c - 1 = \frac{1}{\pi}\int_{-\pi/2}^{\pi/2} dt\, \mathrm{th}\frac{\beta(z-\sin t)}{2kT}, \qquad (3)$$

where c is the number of electrons per unit. Numerical calculations using formulae (2) and (3) show that, as the temperature is lowered, the susceptibility tends to the Pauli value, passing through a maximum at which $\eta = 0.089$ for c = 0.5 (complexes I and II) and $\eta = 0.24$ for c = 1 (complex III). The difference between this case and the preceding one lies in the accuracy of the determination of the position of the maximum.

B. The Low-temperature Region

It is impossible to obtain the increase in susceptibility at low temperatures, either for a regular chain of localized electrons described by the Hamiltonian (1), or for noninteracting electrons in a periodic lattice. In the first case, as T → 0, the susceptibility $\chi \to$ const for $J_m = J_0$,[11] and $\chi \to 0$ for periodic alternation of the interaction.[12] In the second case, as is well-known, the quantity χ is finite for T → 0. We shall show that, in both models, the low-temperature increase in susceptibility can arise as a result of irregularity of the lattice. However, the properties of these two models turn out to be qualitatively different in some respects, and this makes it possible to make an unambiguous choice in favor of one of them.

1. We shall consider a system with Hamiltonian (1), in which the parameters J_m are random quantities. The reason for the growth of χ as T → 0 is easily understood if we assume for the moment that the random quantities J_m can take arbitrarily small values. This means that, in a random way, interaction between certain spins is absent, i.e., the J_m for different m are uncorrelated: $J_m = 0$ with probability c and $J_m > 0$ with probability 1 − c. Then the whole system of spins can be divided into noninteracting subsystems, among which are subsystems with an odd number of spins. Such subsystems at low temperatures are equivalent to a set of a certain number of noninteracting half-integer spins-½ and their susceptibility for T → 0 is described by a Curie law $\chi \sim c/2T$.[13]

In systems with a distribution function $W(J) \to 0$ for $J \to 0$, the singularity in the susceptibility as T → 0 may be conserved, but the increase in χ will be weaker than T^{-1}. We note that such a situation cannot arise in two- and three-dimensional lattices, since here the probability of the appearance of a subsystem weakly interacting with the rest of the system is negligibly small.

By going over from the spin operators S_m to the Fermi operators a_m and a_m^+,[14] we can convert the Hamiltonian (1) to the form

$$\mathscr{H} = \mathscr{H}_1 + \mathscr{H}_2,$$

$$\mathscr{H}_1 = -{}^1/{}_2 N g\mu_B H + \sum_m [J_m(a_m^+ a_{m+1} + a_{m+1} a_m) + g\mu_B H a_m^+ a_m], \qquad (4)$$

$$\mathscr{H}_2 = \sum_m J_m({}^1/{}_2 - a_m^+ a_m)({}^1/{}_2 - a_{m+1}^+ a_{m+1}),$$

where N is the number of spins.

The term $\mathscr{H}_1$ in (4) corresponds to the XY model for the spin Hamiltonian. It is equivalent to a system of free spinless Fermi particles with energies $\epsilon_\alpha + g\mu_B H$, where ϵ_α are the eigenvalues of the Jacobi matrix A_{mn}

with $A_{m,m+1} = A_{m+1,m} = J_m$ and $A_{mn} = 0$ for $n \neq m \pm 1$. The chemical potential of these Fermi particles is equal to $-g\mu_B H$; it determines their number, and from the relation

$$S_z = \sum_m S_m{}^z = \frac{1}{2}N - \sum_m a_m{}^+ a_m \qquad (5)$$

it also determines the z-component of the total spin of the system.

The quantities J_m are random; we therefore introduce the density of the eigenvalues ϵ_α of the matrix A_{mn}, namely the function $\rho_0(\epsilon) = \rho_0(-\epsilon)$. From (4) and (5), we have for the magnetic moment and free energy of of the system

$$M(T,H) = g\mu_B N\left\{\frac{1}{2} - \int_{-\infty}^{\infty} \rho_0(\varepsilon)\left[1 + \exp\frac{\varepsilon + g\mu_B H}{kT}\right]^{-1} d\varepsilon\right\}, \qquad (6)$$

$$F(T,H) = -kTN\int_{-\infty}^{\infty} \rho_0(\varepsilon)\ln\left\{1 + \exp\left[-\frac{\varepsilon + g\mu_B H}{kT}\right]\right\}^{-1} d\varepsilon. \qquad (7)$$

The term $\mathscr{H}_2$ in the Hamiltonian (4) corresponds to the Ising model and describes the interaction between the Fermi particles. As in the Landau[15] theory of Fermi liquids, we shall assume that the weakly excited states of the system (4) can be described by means of Fermi quasi-particles, the density of states of which is determined by the function $\rho(\epsilon, T) = \rho(-\epsilon, T)$, and that at low temperatures we can neglect the dependence of ρ on T. By making this assumption, at low temperatures we obtain, in the case of the Heisenberg Hamiltonian also, the expressions (6) and (7), in which $\rho_0(\epsilon)$ must be replaced by the unknown function $\rho(\epsilon) \neq \rho_0(\epsilon)$.

The function $\rho(\epsilon)$ can be determined from the experimental data on the temperature dependence of the susceptibility. From Eq. (6),

$$\chi(T) = g^2\mu_B{}^2 N\int_0^\infty dx\, \rho(2xT)/\mathrm{ch}^2\, x. \qquad (8)$$

On the other hand, in the temperature range 0.1–10°K, the experimental results are well described by the law

$$\chi(T) \backsim T^{-\alpha} \qquad (9)$$

with $0 < \alpha < 1$ (see Fig. 3). Comparing Eqs. (8) and (9), we obtain for the density of states in the energy interval $0.1°\mathrm{K} \lesssim \epsilon/k \lesssim 10°\mathrm{K}$

$$\rho(\varepsilon) = Ak^{-1+\alpha}\varepsilon^{-\alpha}. \qquad (10)$$

Now, the dependence of the magnetization M on T and H is given by the expression

$$M(T,H) = g\mu_B NAT^{1-\alpha} f_\alpha\left(\frac{g\mu_B H}{kT}\right), \qquad (11)$$

$$f_\alpha(y) = \mathrm{th}\, y \cdot \int_0^\infty x^{-\alpha}\left(1 + \frac{\mathrm{ch}\, x}{\mathrm{ch}\, y}\right)^{-1} dx.$$

From Eq. (11), we have, in the limiting case of weak fields $g\mu_B H \ll kT$,

$$M(T,\ H) = \chi(T)H,$$

$$\chi(T) = 2(1 - 2^{1+\alpha})\Gamma(1-\alpha)\zeta(-\alpha)k^{-1}Ag^2\mu_B{}^2 NT^{-\alpha}, \qquad (12)$$

where $\Gamma(x)$ is the gamma function, and $\zeta(x)$ is the Riemann function. In the limit of strong fields $g\mu_B H \gg kT$, we obtain a power dependence for the moment on the field:

$$M(0,\ H) = (1-\alpha)^{-1} g\mu_B NA(g\mu_B H/k)^{1-\alpha}, \qquad (13)$$

as is also observed experimentally (Fig. 4).

Complex	α from $\chi(T)$	α from M(H)	A from $\chi(T)$, $(°\mathrm{K})^{\alpha-1}$	A from M(H), $(°\mathrm{K})^{\alpha-1}$
I	0,73	0,75	$1.48\cdot10^{-3}$	$1,41\cdot10^{-3}$
II	0,74	0,71	$1.90\cdot10^{-3}$	$1,90\cdot10^{-3}$
III	0,58	0.58	$4,41\cdot10^{-3}$	$4,68\cdot10^{-3}$

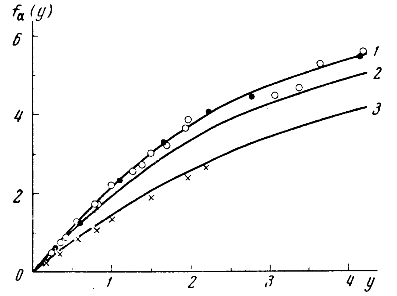

FIG. 5. Graphs of the function $f_\alpha(y)$, with experimental values of the quantity $M(H, T)/g\mu_B NAT^{1-\alpha}$ for complexes I–●, II–○, III–X. Curve 1–α = 0.75, 2–α = 0.71, 3–α = 0.58.

In the table, we compare the parameters α and A obtained from the data on the dependence of χ on T and of M on H shown in Figs. 3 and 4. It is clear that formula (11) describes well the experimental data in the limiting cases of weak and strong fields (the relative errors in the determination of α and A amount to about 2%). To check it in the intermediate region $g\mu_B H \sim kT$, graphs of the functions $f_\alpha(y)$ have been constructed numerically (Fig. 5), and on these graphs we have drawn the experimental values of the quantity $M(H, T)/g\mu_B NAT^{1-\alpha}$ with the parameters α and A determined from the data on the dependence of M on H. Figure 5 shows that formula (11) describes the experimental results with an accuracy of not less than 10% in the whole range of variation of the parameter $g\mu_B H/kT$.

2. We shall consider the alternative model of noninteracting electrons in an irregular one-dimensional lattice. For the reasons described in Sec. 3A, we can seek the spectrum of the electrons of the chain in the tight-binding approximation. Then, as in the XY model, the density of single-particle states will be determined by the density of the eigenvalues of the Jacobi matrix with $A_{m,m+1} = A_{m+1,m} = \beta_m \leq 0$, where β_m is the resonance integral for the electron transition from molecule m to molecule m + 1. In an irregular lattice, β_m are random quantities, and if we assume that the resonance integral β_m can take arbitrarily small values with finite probability c, the Jacobi matrix A_{mn} is decomposed into blocks, unconnected with each other and consisting of Jacobi matrices of finite order. In this case, at the center of the band we obtain a singularity in the density of states of the form $c\delta(\epsilon)/2$, since Jacobi matrices of odd order always have a zero eigenvalue. One might think that the singularity of the function $\rho_0(\epsilon)$ at zero is conserved, but will be weaker, if the distribution function $W(|\beta|) \to 0$ as $\beta \to 0$. However, this singularity is manifested in the thermodynamic properties of the electrons only in the case when the Fermi level is positioned at the same point as this singularity.

In simple salts with one unpaired electron per molecule (complex III), we are dealing with precisely this situation. Then, at low temperatures, the system of electrons will be described by the expressions (6) and (7), in which the right-hand sides must be doubled, with g replaced by g/2 in them. By taking again the density of states in the form (10), we obtain, as in the localized-electron model also, power dependences for χ on T and for M on H. But now the parameters A, calculated from the data on the dependences of χ on T and of M on H, will differ by a factor 2^{α} (~1.5 for complex III). Thus, for the highly conducting salts, it would also be possible, to an accuracy within the factor 2^{α}, to describe the experimental data in the framework of the model of noninteracting electrons.

In the complex salts (complexes I and II), there is one unpaired electron for every two TCNQ molecules, and X-ray structural investigations, which, admittedly, are performed at room temperature, show that in the highly conducting complexes all the distances between neighboring TCNQ molecules are the same.[4] The electron band must be only one-quarter occupied, and the Fermi level must be positioned in a region where there are no singularities in the density of states. Thus, in the noninteracting-electron model, it is impossible to explain the experimentally observed low-temperature magnetic properties of the complex salts.

4. DISCUSSION

The interpretation of the results in Sec. 3B is based essentially on two assumptions. First, we assumed that the Hamiltonian (4) with a random interaction parameter can lead to a density of states with a singularity of the required type. Secondly, it was assumed that the excitation spectrum of such a Hamiltonian has a Fermi-liquid character.

1. In the XY model, the density of states of the Fermi particles coincides with the density of eigenvalues of the Jacobi matrices, of which the non-zero elements $A_{m,m+1} = A_{m+1,m} = J_m$. If the uncorrelated random quantities J_m can take zero values with finite probability, then as was shown above, this will lead to a singularity in the density of states of the form $c\delta(\epsilon)/2$. The exact result obtained by Dyson[16] for the density of eigenvalues of the Jacobi matrix whose elements $A_{m,m+1} = A_{m+1,m} = J_m$ are uncorrelated and are specified by a distribution function of the form

$$W_n'(J) \equiv \frac{d}{dJ} W_n(J) = [2n^n/(n-1)!]\,(J/J_0)^{2n-1} \exp(-nJ^2/J_0^2), \quad n=1, 2, \ldots \tag{14}$$

corroborates the argument that, if W(J) → 0 for J → 0, the singularity in the density of states is conserved, but becomes weaker.

The density of states found by Dyson for finite n as $\epsilon \to 0$ has a singularity of the form

$$\rho_0(\varepsilon) \infty \varepsilon^{-1} |\ln(\varepsilon/J_0)|^{-3}, \tag{15}$$

as a result of which, the susceptibility in the XY model for T → 0 increases according to the law

$$\chi(T) \infty T^{-1} |\ln(kT/J_0)|^{-2}. \tag{16}$$

The distribution function densities (14) tend to zero as J → 0, but the singularities in (15) and (16) are, nonetheless, very strong. We note that Dyson's solution was applied in [17] to describe the thermodynamic properties of an XY model with randomly distributed interaction parameters; however, the appearance of a new singularity at H = 0, T = 0 remained unnoticed.

In the one-dimensional Ising model with antiferromagnetic interaction, the susceptibility is given by the expression

$$\chi(T) = \frac{1}{4} \frac{g^2 \mu_B^2 N a(T)}{2 - T a(T)}, \quad a(T) = \int_0^\infty (1 - \operatorname{th} x) W'(Tx)\, dx, \tag{17}$$

and $\chi \to \infty$ as T → 0 only when W′(J) → ∞ as J → 0. This result is connected with the existence in the Ising model of an excitation gap determined by the minimum value of the parameter J_m. In the Heisenberg model, as in the XY model, there is no gap in the excitation spectrum of a regular chain. Therefore, in a real crystal, a distribution function falling off even faster than (14) as J → 0 can lead to the singularity (10), since this singularity is weaker than the singularity (15).

2. We cannot justify theoretically the assumption, necessary to obtain expressions (6), (7) and (11), on the Fermi-liquid character of the excitation spectrum of the Hamiltonian in (4), in which the J_m are random quantities. However, this assumption is completely natural, since for a linear chain with uniform interaction $J_m = J_0$, the results obtained in the Hartree-Fock approximation and in the Landau Fermi-liquid approximation agree well with the results of exact calculations.[18] The fact that expression (11) describes the experimental data surprisingly well can also serve as a justification of this assumption. In fact, the coefficients of $T^{-\alpha}$ and $H^{1-\alpha}$ in the relations (12) and (13) were obtained by assuming that the spectrum of the Hamiltonian (4) has a Fermi character, and the agreement of the parameters A determined from the experimental data for $\chi(T)$ and M(0, H) is evidence in favor of this assumption.

We note that the assumption of Fermi character of the spectrum of the elementary excitations of a starting Hamiltonian with strong interaction of the electrons—a Hamiltonian of the Hubbard type—would certainly be invalid, at least in the case of the complex with phenazine. In fact, an exact solution for a Hubbard Hamiltonian with the number of electrons equal to the number of centers [19] shows that there is always a gap in the single-particle spectrum of the system. Therefore, the weakly excited states of such a system cannot be described in the framework of a Fermi-liquid model with quasi-particles corresponding to the electrons.

3. It is of interest to make a further experimental check on the results stemming from the assumptions made to explain the low-temperature magnetic properties of the complexes. Measurements of the electronic heat capacity c and entropy σ at low temperatures can provide this additional check. Expressions for c and σ can be obtained from (7), by replacing $\rho_0(\epsilon)$ by the function $\rho(\epsilon, T)$. Neglecting the quantity $\partial\rho(\epsilon, T)/\partial T$ for small T and taking (10) for $\rho(\epsilon)$, we obtain at low temperatures:

$$c(T, 0) = (1-\alpha)\sigma(T, 0) = 2(1 - 2^{\alpha-1})\Gamma(3-\alpha)\zeta(2-\alpha) ANkT^{1-\alpha} \tag{18}$$

and for $g\mu_B H \gg kT$,

$$c(T, H) = \sigma(T, H) = {}^1/_3\pi^2 ANkT (g\mu_B H/k)^{-\alpha}. \tag{19}$$

It can be seen from Eqs. (18) and (19) that the heat capacity and entropy of the electron system are reduced by imposing a strong magnetic field $g\mu_B H \gg kT$, and this decrease is greater the stronger the field H.

4. The question of the causes of irregularities in a linear chain of TCNQ molecules is not completely clarified at the present time. It is obvious that the cause might be the presence of defects weakening the interaction between neighboring spins. The good reproducibility of the low-temperature increase in susceptibility for different samples of the same complex could thus be connected with the equivalent conditions used in obtaining the samples, leading to the same concentration of defects in them. However, the attempts which we made specifically to observe the influence of the temperature at which the samples crystallized (+86°C and −5°C) on the magnitude and behavior of the susceptibility of complex II at low temperatures did not give a positive result.

5. CONCLUSION

1. The features of the magnetic properties of highly conducting complexes at low temperatures force us, evidently, to reject a description of these systems in the framework of the one-electron approximation in favor of a model of localized electrons. We note that the electron-phonon interaction and, primarily, the polarization, by an electron, of the TCNQ molecule at which it is situated can lead to the formation of a polaron of the "molecular" type, similar to that which has been observed in crystals of molecular sulfur.[20] Since the polaron effect leads to an effective decrease of the electron transition integral from molecule to molecule, it facilitates the localization of electrons by the Coulomb repulsion. In this case, the conduction will be by a hopping mechanism and the behavior of the thermal electromotive force of the highly conducting TCNQ complexes[21] is indeed evidence that the conduction is likely to be of this type.

2. In the work of Dzyaloshinskiĭ and Larkin,[2] it is predicted that a quasi-one-dimensional system of electrons can exist in three states: metallic, superconducting and antiferromagnetic. A state with localized electrons (a "Mott" insulator) corresponds to the third possibility, since for this state the spin structure of the electrons is described by a Heisenberg Hamiltonian with antiferromagnetic interaction. (So long as the spin correlation functions of the Heisenberg Hamiltonian remain unknown even at T = 0, this state may only formally be called antiferromagnetic.) However, a state with localized electrons is realized only when there is strong interaction between the electrons, and therefore it cannot be described in the framework of the approximation[2] developed for weakly interacting electrons.

3. The fractional-power dependences of the susceptibility and magnetization on the temperature and field respectively, observed in TCNQ complexes at low temperatures, are, apparently, the first experimentally established manifestation of a singularity in the density of states of one-dimensional disordered systems. It should also be possible to observe an analogous singularity in the density of one-electron states in one-dimensional metals with half-filled bands, if such metals can be created.

The authors thank M. L. Khidekel' and É. B. Yagubskiĭ for preparing the samples, and A. I. Larkin, M. M. Mikulinskiĭ, E. I. Rashba and D. I. Khomskiĭ for useful discussion of the work.

Note added in proof (December 20, 1971). 1) In the recent paper by A. J. Epstein, S. Etemad, A. F. Garito and A. J. Heeger (Solid St. Comm. 9, 1803 (1971)), a low-temperature increase in susceptibility weaker than that given by our data was noted. This is less likely to be connected with a difference in the purity of the samples, as the above authors believe, than with the difference in the method of measurement. The fact that balance measurements do not coincide with data obtained by means of EPR was also noted in the papers by K. Hirakawa and Y. Kurogi (Suppl. Progr. Theor. Phys. 46, 147 (1970)) and M. Date. H. Yamazaky, M. Motokawa and S. Tazawa (Suppl. Progr. Theor. Phys. 46, 194 (1970)). 2) The heat capacity measurements performed by Epstein et al. for the complex (NMePh)(TCNQ) make it possible to check that formula (18) is fulfilled. The temperature dependence of the heat capacity cited in their work can bee represented in the form of a sum of a lattice part and a part varying with temperature like $T^{1-\alpha}$ with $\alpha = 0.58$. The value of A obtained by this procedure agrees within 25-30% with those given in the table.

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Translated by P. J. Shepherd
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