

# Paramagnetism of the high-conductivity TTF-TCNQ crystals

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We calculate the paramagnetic susceptibility of high-conductivity donor-acceptor crystal TTF-TCNQ. From the magnetic point of view, the entire crystal breaks up into a number of noninteracting antiferromagnetic planes. Using earlier calculations,<sup>[1]</sup> we determine the degree of charge transport in this system. It is characterized by the quantity  $\rho = 2/3$ .

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In<sup>[1]</sup> we investigated the charge state of the highly-conducting donor-acceptor molecular crystal TTF-TCNQ. In particular, it was found that in the ground state this crystal constitutes a set of TTF<sup>+</sup> and TCNQ<sup>-</sup> ions as well as neutral TTF and TCNQ molecules. Furthermore, the number  $\rho$  of electrons transferred from the TTF donor molecules (*D*) to the TCNQ acceptor molecules (*A*), divided by the total number *A*, certainly lies in the range  $\frac{1}{4} \leq \rho \leq \frac{2}{3}$ . (The value  $\rho = 1$  is thus excluded.) As noted in<sup>[1]</sup>, the TTF-TCNQ system is characterized by the following circumstance: the energies of the electronic states of the individual molecules

and the electrostatic energy of the crystal (per molecule) exceed by at least one order of magnitude the energy connected with the intermolecular electron hopping. This enables us to neglect the kinetic energy of the electrons.<sup>[1]</sup> However, when the spin properties are considered, it is necessary to go beyond the framework of this approximation, since the ground state calculated with the hopping neglected is degenerate in the spin, and to lift this degeneracy it is necessary to take into account the kinetic energy of the electrons.

The present article is devoted to the spin properties

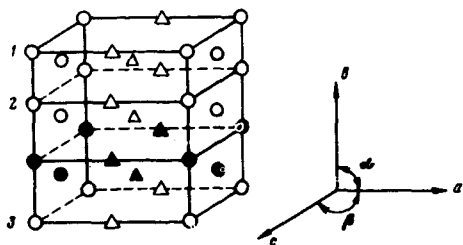


FIG. 1. Lattice of the TTF-TCNQ crystal. Arrangement of ions and molecules for  $\rho = \frac{2}{3}$ .  $\Delta$ ,  $\circ$ —centers of the TCNQ<sup>-</sup> and TTF<sup>+</sup> ions, respectively;  $\blacktriangle$ ,  $\bullet$ —centers of the corresponding molecules.  $\alpha = 90^\circ$ ,  $\beta = 104^\circ 46'$ ,  $a = 12.298 \text{ \AA}$ ,  $b = 3.819 \text{ \AA}$ ,  $c = 18.468 \text{ \AA}$ .

of the TTF-TCNQ crystal. This study is of interest, in particular, in connection with measurements of the electron spin susceptibility of this crystal, which were carried out in<sup>[21]</sup>.

The total electron Hamiltonian of the system in question can be written in the form<sup>[11]</sup>:  $\hat{H} = \hat{H}_0 + \hat{H}_1$ , where  $\hat{H}_0$  is the operator of the electrostatic energy of the crystal together with the terms describing the electronic states of the individual molecules— $A$  and  $D$ ; the ground state energy  $\hat{H}_0$  was calculated in<sup>[11]</sup>.  $\hat{H}_1$  is the kinetic-energy operator. An analysis of the geometrical structure of TTF-TCNQ crystals<sup>[3]</sup> (see Fig. 1) shows the electron hopping along the  $c$  axis can be neglected (the corresponding resonance integrals are negligibly small), and  $\hat{H}_1$  describes a system of noninteracting planes constructed on the vectors  $a$  and  $b$  ( $b$  is the direction of maximum conductivity).

Application of the theory of the perturbations of the degenerate level (see, e. g.,<sup>[4]</sup>) leads in second order in  $\hat{H}_1$  to the effective spin Hamiltonian, the spins being localized on the ions  $A$  and  $D$ , while the form of the spin Hamiltonian depends on  $\rho$ . On the other hand, according to<sup>[11]</sup>,  $\rho$  lies in the interval from  $\frac{1}{4}$  to  $\frac{2}{3}$ . This uncertainty in the value of  $\rho$  can, however, be eliminated by using the following reasoning: Consider, for example, the case  $\rho = \frac{1}{2}$ . As seen from Fig. 2a, in this case the spin system consists of noninteracting antiferromagnetic strings and its susceptibility differs from zero at  $T = 0$ .<sup>[5]</sup> According to<sup>[2]</sup>, on the other hand, the paramagnetic susceptibility  $\chi$  of the TTF-TCNQ crystal tends to zero as  $T \rightarrow 0$  like  $\chi \sim \exp(-\Delta E/kT)$  ( $\Delta E \approx 84 \text{ }^\circ\text{K}$ ). Similar arguments for other values of  $\rho$  lead to the conclusion that the value of  $\rho$  for which  $\chi \rightarrow 0$  exponentially as  $T \rightarrow 0$  is  $\rho = \frac{2}{3}$ . A similar behavior

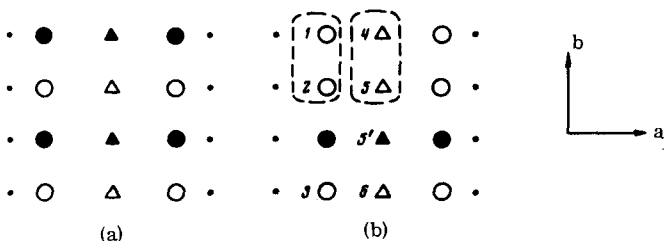


FIG. 2. Arrangement of the ions and molecules in the  $ab$  plane; a)  $\rho = \frac{1}{2}$ , b)  $\rho = \frac{2}{3}$ .

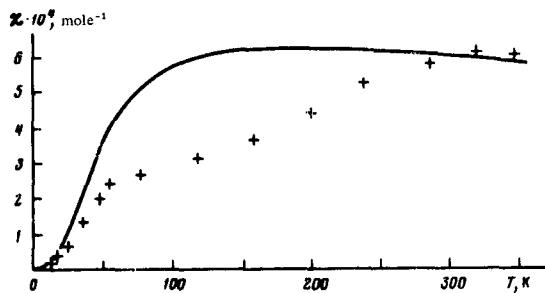


FIG. 3. Temperature dependence of the spin susceptibility: solid curve—calculated from formula (9), crosses—experimental data.<sup>[22]</sup>

for  $\chi$  will take place also at  $\rho = \frac{4}{5}$ , but  $\rho = \frac{4}{5}$  lies outside the confidence interval obtained for  $\rho$  in<sup>[11]</sup>. As seen from Fig. 2b, the system is in this case two-dimensional antiferromagnet with the maximum value of the exchange integral for the spins localized on pairs of neighboring ions  $D$  and  $A$  (shown by the dashed lines in Fig. 2b). Since triplet excitations of the quasimolecules ( $A_2^-, D_2^+$ ) made up of these pairs are separated by a gap from the ground singlet state, the spin susceptibility of such a system will become exponentially small as  $T \rightarrow 0$ .

The effective spin Hamiltonian is of the form

$$\begin{aligned} \tilde{H} = & J_D \sum_{ij} S_{2i-1, 2j-1} S_{2i, 2j-1} + J_A \sum_{ij} S_{2i-1, 2j} S_{2i, 2j} \\ & + J_{AD} \sum_{ij} S_{i,j} S_{i,j+1} + J_{DD} \sum_{ij} S_{2i, 2j-1} S_{2i+1, 2j-1} \\ & + J_{AA} \sum_{ij} S_{2i, 2j} S_{2i+1, 2j} \end{aligned} \quad (1)$$

where  $J_D$ ,  $J_A$ ,  $J_{AD}$ ,  $J_{DD}$ , and  $J_{AA}$  are exchange integrals for the spins (1), (2); (4), (5); (1), (4); (2), (3); and (5), (6) (Fig. 2b), respectively, and the summation is carried out over the lattice sites occupied by the ions. The last two terms in (1) correspond to fourth-order perturbation theory in  $\hat{H}_1$ . The exchange integrals  $J$  can be expressed in the usual manner in terms of the electronic parameters of the system.

Thus, for example, for  $J_A$  and  $J_{AA}$  we have

$$\begin{aligned} J_A = & 4\beta_1^2 \Delta^{-1}(4,5); \quad J_{AA} = 4\beta_1^4 [\Delta^{-2}(5',5) \Delta^{-1}(5,6) \\ & + 2\Delta^{-2}(5',5) \Delta^{-1}(5',5',6)] \end{aligned} \quad (2)$$

where, in accordance with the notation of Fig. 2b,  $\Delta(4, 5)$  is the increment of the unperturbed energy  $\hat{H}_0$  due to the transport of the electron from (5) to (4),  $\Delta(5', 5; 5', 6)$  is the increment due to the transport of electrons from (5) and (6) to (5'), etc., while  $\beta_1$  is the resonant integral of the quasimolecule  $A_2^-$ . Introducing the operators for the creation and annihilation of triplet excitations of quasimolecules, we can reduce the Hamiltonian (1) to the Hamiltonian of the interacting spin waves.<sup>[6]</sup> At low temperatures, the spin waves are subject to Boltzmann statistics, and the interaction between them can be neglected, since their density is low. The spin-wave spectrum is of the form

$$\epsilon(k) = J + \frac{J_1}{2} \cos k_b + J_2 \cos k_a, \quad (3)$$

where  $k_a$  and  $k_b$  are the quasimomenta in the directions of  $a$  and  $b$ , respectively. Since the form of the spectrum does not depend on the concrete values of the exchange integrals, we have assumed in (3) that  $J = J_A = J_D$  and  $J_1 = J_{AA} = J_{DD}$ ; ( $J_2 = J_{AD}$ ).

Using (3) with  $T \rightarrow 0$ , we obtain for the susceptibility  $\chi$  of the pair  $AD$

$$\chi = \frac{4}{3} \frac{(\mu g)^2}{\pi \sqrt{2 J_1 J_2}} \exp\left(-\frac{J - J_2 - J_1/2}{kT}\right). \quad (4)$$

From a comparison of (4) with the experimental data in the low-temperature region we obtain  $J/k = 800^\circ\text{K}$ ,  $J_1/k = 77.2^\circ\text{K}$ , and  $J_2/k = 677.6^\circ\text{K}$ .

To calculate  $\chi$  in the entire temperature region, we employ an approximate formula obtained under the assumption that excitations of the spin-wave type satisfy independent triplet statistics (strictly speaking, this can be justified only in the one-dimensional case<sup>[6]</sup>), and also neglect their scattering. We then obtain  $\chi$  by calculating a two-dimensional integral:

$$\chi = \frac{4}{3} \frac{(\mu g)^2}{kT\pi^2} \int_0^\pi \int_0^\pi dk_a dk_b (3 + \exp(\epsilon(k_a, k_b)/kT))^{-1}. \quad (5)$$

As seen from Fig. 3, the susceptibility calculated by us agrees with the experimental data at low and at high temperatures. As to the discrepancy between the calculated and experimental data at  $50^\circ\text{K} \lesssim T \lesssim 200^\circ\text{K}$ , it can be attributed, first, to the approximate character of (5) and, second, to the fact that the conduction electrons were not taken into account in our analysis.

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