

# Nuclear antiferromagnetic change with indirect exchange interaction in the organic complex dibenzotetrathiofulvalene- $I_3$ (DBTTF- $I_3$ )

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The magnetic susceptibility and conductivity of the organic quasi-one-dimensional salt dibenzotetrathiofulvalene- $I_3$  are studied in the temperature range 1.3–360 K. The Hubbard model in the  $U \gg t$  limit is used to analyze the experimental data ( $U$  is the energy of the Coulomb repulsion between the electrons of a single molecule and  $t$  is the transition integral between the molecules). It is shown that the magnetic susceptibility can be satisfactorily described by an infinite regular linear chain with indirect antiferromagnetic exchange interaction via the iodine atoms. Estimates yield  $U = 4040$  K and  $t = 450$  K.

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## INTRODUCTION

The great recent interest in the study of quasi-one-dimensional organic compounds is due, first to the potential feasibility of synthesizing organic metals<sup>1</sup> and semiconductors,<sup>2</sup> and second to the possibility of significantly altering the physical properties of compounds by even an insignificant variation of the cation or anion. The latter is due either to a change in the degree of charge transfer, or to the appearance of incommensurability of the sublattices, or else to a complete change of the structure.<sup>3,4</sup> By now, many compounds have been synthesized, more or less chemically and structurally similar to the ion-radical tetrathiofulvalene-tetracyanoquinodimethane (TTF-TCNQ), which has now become classical. As a rule, the crystals of most of these substances grow along stacks of cations and anions, and in rare cases perpendicularly to this direction.<sup>5</sup> The latter type of compound is of considerable interest for research, since the packing of the molecules in the crystal establishes in the main the physical properties of the complexes.

We report here on the magnetic susceptibility and conductivity of the cation-radical salt dibenzotetrathiofulvalene-iodine (DBTTF- $I_3$ ), the crystal-growth axis of which is perpendicular to the axis of the stack of cations and anions. The complex DBTTF- $I_3$  was obtained by reaction of DBTTF with  $I_3$  in an acetonitril or nitrobenzene solution at initial-reagent ratios 1:1 and 1:0.25, respectively.<sup>6</sup>

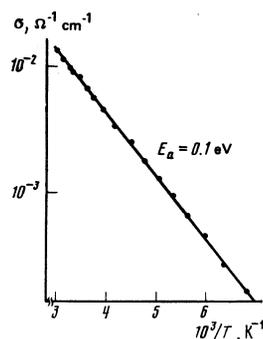


FIG. 1. Temperature dependence of the conductivity.

## RESULTS OF EXPERIMENT

The electric conductivity of the DBTTF- $I_3$  salt was measured by a dc four-contact method in single crystals with typical dimensions  $0.2 \times 0.3 \times 2$  mm. Outwardly these are four parallelepipeds with metallic luster. The conductivity measured along the long axis was  $2 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$ . Its temperature dependence is shown in Fig. 1. It can be seen that in the temperature range 150–160 K the conductivity varies in accord with an activation law with an activation energy 1120 K (0.1 eV).

The magnetic susceptibility was measured with a magnetic balance of the Faraday type in the temperature range 1.3–360 K. With decreasing temperature the susceptibility increases monotonically, reaches a maximum at 120 K, and at helium temperatures there appears the low-temperature tail typical of all ion-radical quasi-one-dimensional salts.<sup>7</sup> If the low-temperature growth obeys the Curie law, it is customarily used to assess the impurity content of the compound. The investigated salt should be regarded as quite pure, since the low-temperature susceptibility growth is very small and corresponds to a paramagnetic impurity density 0.05%. The diamagnetic susceptibility was determined by the Pascal rule and amounted to  $338 \times 10^{-6} \text{cm}^3/\text{mol}$ . Figure 2 shows the temperature dependence of the paramagnetic susceptibility after subtracting the low-temperature increase and the small ferromagnetic contribution ( $7 \times 10^{-6}$ ).

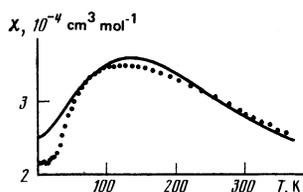


FIG. 2. Dependence of the magnetic susceptibility on the temperature after subtracting the ferro- and paramagnetic impurities. The solid ( $J = 100$  K) curve was obtained from the formula proposed in Ref. 18 and the points are experimental.

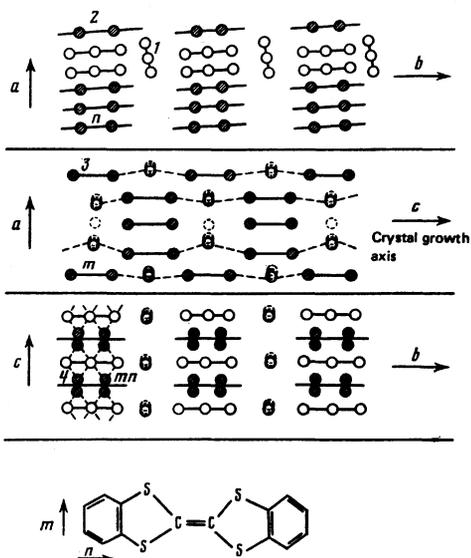


FIG. 3. Three schematic projections along the axes  $c$ ,  $b$ , and  $a$  of the DBTTF- $I_3^-$  complex. 1) The  $I_3^-$  anion, 2, 3, 4) the three projections of the DBTTF cation.

## DISCUSSION OF RESULTS

From the formula of the compound it was expected that the room-temperature susceptibility would correspond approximately to one spin per molecule, but the measurement showed that it is less than one-third this value. It can also be seen from Fig. 2 that at the lowest temperature the paramagnetic susceptibility does not decrease to zero, as is most frequently the case in one-dimensional organic compounds after the impurity contribution is subtracted, but tends to a certain constant value.<sup>8</sup> These results can be understood by analyzing the x-ray structure data on the DBTTF- $I_3^-$  salt.<sup>9</sup> Three projections along the axes  $c$ ,  $b$ , and  $a$  are shown schematically in Fig. 3. It can be seen that in this case that the plane-to-plane packing of the molecules into infinite stacks along the  $a$  axis, which is typical of one-dimensional conducting salts, does not exist in this case. The chain breaks up here along this axis into triads of DBTTF molecules alternating with two iodine triads. Inside the triads, between the sulfur atoms, of the DBTTF molecules there are shortened 3.5 Å contacts. It is noted also in Ref. 9 that along the  $c$  axis there are shortened intermolecular contacts between the sulfur atoms of the first and third molecules of the DBTTF triad and the atoms of the anion  $I_3^-$  of the neighboring stack. The presence of shortened contacts between the sulfur and the iodine is apparently the reason why the crystal growth axis (the  $c$  axis) lies in the plane of the DBTTF molecules and not perpendicular or at a large angle to it, as is typical of most one-dimensional conducting salts.

The presence in the chain along the  $a$  axis of triads made up of DBTTF molecules explains qualitatively the value of the magnetic susceptibility at room temperature. Assuming between the nearest neighbors of the triad the presence of a strong coupling approximately equal to the exchange in the linear chain of the salt DBTTF<sub>2.67</sub>SnCl<sub>6</sub> (Ref. 10),<sup>11</sup> we can use in rough approx-

imation for this triad the results of the calculation of the molecular orbitals by the Huckel method for the three-center  $H_3$  molecule. In this approximation we find that for the three electrons possessed formally by the triad of the DBTTF molecule, two are paired and are on the middle molecule, and one electron is located with equal probability at the first or third molecule of the triad. This fact can explain the decrease of the susceptibility of the investigated salt by a factor of three compared with the expected value.

To interpret the temperature dependence of the magnetic susceptibility we use the Hubbard model, which includes the Coulomb repulsion energy  $U$  of two electrons when they are located on one molecule, and the transition integral (or resonance integral)  $t$  between neighboring molecules. The quantity  $t$  contributes to delocalization of the electrons with production of a band, whereas the quantity  $U$  leads to localization on the sites owing to the electron-electron repulsion. The total temperature dependence of the magnetic susceptibility was calculated within the framework of this model only in the two limiting cases  $U \gg t$  and  $U \ll t$  (Refs. 11 and 12). Klein and Seitz<sup>12</sup> have shown that for the case  $U \gg t$  the spin-dependent part of the Hubbard Hamiltonian can be expressed in terms of a Heisenberg interaction with an effective exchange integral in the following manner:

$$J = (2t^2/U)\rho(1 - \sin 2\pi\rho/2\pi\rho), \quad U \gg t, \quad (1)$$

where  $\rho$  is the degree of charge transfer or the average number of unpaired electrons per site.

The question of the degree of charge transfer from a donor to an acceptor in conducting one-dimensional organic salts is not yet completely clear. According to some workers<sup>13</sup> the transfer is almost complete in a number of organic salts, while others<sup>14</sup> state that the transfer in the same salts is far from complete. In principle,  $\rho$  can be determined from the diffuse x-ray scattering with wave vector  $2k_F$  (Ref. 15). The degree of transfer in the investigated salt can be indirectly assessed from the properties of the anion and of the cation. For certain salts with DBTTF cation the charge transfer from the donor to the acceptor is complete.<sup>10</sup> It is known also that salts with iodine tend to produce  $I_3^-$  triads.<sup>16</sup> It can be assumed that the energy transfer in the salt investigated here is also complete.

If the charge transfer is complete ( $\rho = 1$ ), the one-dimensional Hubbard model with half-occupied band becomes equivalent, in accord with Eq. (1), to the one-dimensional antiferromagnetic Heisenberg model with exchange integral  $J = 2t^2/U$ . The magnetic susceptibility of the investigated salt can be described in this case by a Heisenberg Hamiltonian for an infinite regular chain of spins with antiferromagnetic interaction, numerical calculations for which were made by Bonner and Fisher,<sup>17</sup> and an approximate formula was proposed by Torrance *et al.*<sup>18</sup> It is seen from Fig. 2 that the experimental points agree satisfactorily with the theoretical curve plotted for a regular chain with an exchange integral  $J = 100$  K.

It should be noted that in a salt with DBTTF-

TCNQCl<sub>2</sub>, which has the same cation radical,<sup>19</sup> the susceptibility at temperatures lower than 38 K also varies in accord with the properties of an infinite antiferromagnetic chain with an exchange integral  $J = 80$  K. The susceptibility of the quasi-one-dimensional salt methylmorpholine-(tetracyanoquinodimethane)<sub>2</sub> (MEM-TCNQ<sub>2</sub>) (Ref. 20) also varies similarly, with an exchange integral  $J = 53$  K. In both cases the transfer of the electron from the donor to the acceptor is incomplete and by exchange is meant antiferromagnetic interaction of identical molecules regularly arranged in stacks with distances 3.3–3.5 Å between nearest neighbors. The exchange-integral values obtained for these salts are quite reasonable.

In the investigated DBTTF-I<sub>3</sub> salt there are no regular stacks with identical neighbors (see Fig. 3). The nearest neighbors, if it is assumed that the electron is mainly localized on sulfur atom of the first and third molecules of the DBTTF triad, are located on the next triad along the  $c$  axis of the crystal, which is separated from the first triad by I<sub>3</sub><sup>-</sup> molecules. The shortest distance between the sulfur atoms is of the order of 7.5 Å. The exchange integral typical of this salt,  $J = 100$  K, is very large. Only indirect exchange via the iodine atoms is possible. It is precisely for these sulfur and iodine atoms that shortened contacts were observed in the structure.<sup>9</sup>

If we start out from the Hubbard model to describe the magnetic properties and the conductivity of the investigated salt we can, knowing the value of the exchange integral  $J = 100$  K and the conduction activation energy  $E_a = 1120$  K, obtain the values  $U$  and  $t$  from the simple system<sup>21</sup>

$$J = 2t^2/U, \quad U \gg t, \quad (2)$$

$$\Delta W = U - 4t.$$

It is assumed here that the Hubbard-model gap  $\Delta W$  leads to an activation dependence of the conductivity on the temperature, and  $\Delta W = 2E_a$ . It follows from (2) that  $t = 450$  K and  $U = 4040$  K. Additional optical measurements might confirm the validity of the results.

It must be noted in conclusion a specific feature of the behavior of the DBTTF-I<sub>3</sub> salt when it is heated. The magnetic susceptibility is described by a regular antiferromagnetic chain up to 360 K, and with further increase of the temperature the susceptibility begins to decrease abruptly. Monitoring the weight of the specimen simultaneously with measurement of the magnetic susceptibility has shown that the substance begins to lose weight at this temperature.

An interesting feature of the behavior of DBTTF-I<sub>3</sub> single crystals was observed when they were heated on the miniature heating stand used to determine the melting temperatures of organic compound. With this instrument the heating of the crystal is directly observed in the microscope drawtube.

The black DBTTF-I<sub>3</sub> single crystals, which have a metallic luster at room temperature, begin to lose their luster at 360 K, and when the temperature is raised to

443 K the iodine becomes completely volatilized and the crystals turns yellow, but without changing shape or size. The yellow crystals obtained after the evaporation of the iodine melt at 515 K, which is the melting temperature of pure DBTTF. The porous DBTTF "crystals" produced by heating to 443 K easily regain their initial conductivity (of the order of  $10^{-2} \Omega^{-1} \text{ cm}^{-1}$ ) if they are placed for several minutes in an iodine atmosphere at room temperature.

It can be assumed that when DBTTF-I<sub>3</sub> single crystals are heated to 443 K the iodine evaporates through channels along the  $b$  axis. This is made quite possible by the structure of the salt (see Fig. 3). It is possible that this leaves a metastable friable lattice of DBTTF molecules. When it is placed in iodine vapor, the channels are again filled with iodine.

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<sup>1</sup>A value 0.3 eV is erroneously cited in Ref. 1 for the band width; the correct value is 0.8 eV.

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