Spin-Peierls transition in the organic complex $(BPDT-TTF)_2I_3$

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A study of the static magnetic susceptibility and of the EPR spectra has shown that at $T > 50$ K the magnetic properties of $(BPDT-TTF)_2I_3$ are well described by the Heisenberg one-dimensional antiferromagnetic model with an exchange integral $J = 170$ K. Below $T = 50$ K, a gap is produced in the spin-excitation spectrum and is due to the alternation of the antiferromagnetic chain. At $T < 10$ a doublet is observed in the EPR spectrum and is due to dipole–dipole interaction of the spins.

INTRODUCTION

The discovery[1] of superconductivity at $T_c = 1.5$ K and normal pressure in the quasi-two-dimensional organic metal β-$(BEDT-TTF)_2I_3$[1] has attracted much attention to research into this class of compounds. Many attempts were made to modify chemically both the anion and the cation parts in β-$(BEDT-TTF)_2I_3$ to obtain new organic superconductors and metals.[2]

The (BPDT-TTF) molecule[3] is the closest analog of (BEDT-TTF), from which it differs by the presence of an extra methylene group in the external heterocycle. The $(BPDT-TTF)_2I_3$[4,5] is fully isostructural with β-$(BEDT-TTF)_2I_3$. Its conductivity, however, is that of a semiconductor.[4] The causes of this striking contrast in the behavior of these compounds are the seemingly small differences between their crystal stacking. The $(BPDT-TTF)_2I_3$ structure, just as that of β-$(BEDT-TTF)_2I_3$, consists of layers of organic molecules alternating with anion layers. In the $(BPDT-TTF)_2I_3$ structure, however, stacks of BPDT–TTF molecules are more pronounced, while dimers of the BPDT–TTF molecules are more pronounced inside the stacks.[4] As a result, the electron spectrum of $(BPDT-TTF)_2I_3$ is more readily quasi-one-dimensional. This follows also from quantum-chemical calculations of the overlap integrals of the neighboring BPDT–TTF molecules.[5]

Since the $(BPDT-TTF)_2I_3$ cation subsystem has a charge + 1 per pair of BPDT–TTF molecules, i.e., an odd number of electrons in the unit cell, it should have, from formal band theory considerations, metallic properties. The gap present then in the electron-excitation spectrum is obviously of the Mott-Hubbard type. On the other hand, there should be no gap in spin-excitations spectrum, i.e., the system should possess paramagnetism.

We deemed it of interest to investigate the magnetic properties of $(BPDT-TTF)_2I_3$ with an aim at casting more light on the character and the nature of the electron interaction in low-dimensionality organic materials. Contributing to the interest in this field is also the presence of a certain analogy between quasi-two-dimensional superconductors, in which a large role is likewise played by Coulomb interactions, and competition is present between antiferromagnetism and superconductivity.[6]

By investigating the static magnetic susceptibility and the EPR spectra in $(BPDT-TTF)_2I_3$, the present study has revealed a magnetic phase transition, possibly of the spin-Peierls type, at $T \approx 50$ K.

EXPERIMENTAL PROCEDURE AND RESULTS

The $(BPDT-TTF)_2I_3$ crystals were obtained by chemical oxidation of BPDT–TTF ($1.27 \cdot 10^{-4}$ mol) by molecular iodine ($0.64 \cdot 10^{-4}$ mol) in 1,1,2-trichlorethane (25 ml) at $t = 105°$ C in an argon atmosphere, followed by a slow ($v = 1.2°$ C/h) cooling of the reacting mixture from $t = 80$ °C to room temperature. The reaction products, BPDT–TTF single crystal with typical dimensions $2 \times 0.5 \times 0.02$ mm, were identified by x-ray diffraction.

The static magnetic susceptibility was measured by the Faraday method in the temperature interval 1.3–300 K. The sample was a set of randomly oriented single crystals with a total mass 40 mg. The $\chi(1/H)$ dependence was measured at room and helium temperature in the field range 2.8–9.6 kOe, and the result revealed a small ferromagnetic impurity contribution corresponding to an iron content 25 ppm in the sample. In addition to this contribution, we subtracted from the measured susceptibility the diamagnetic contribution of the filled electron shells, equal to $5.6 \cdot 10^{-4}$ cm$^3 \cdot$mol^{-1}, determined by the Pascal additive scheme. The paramagnetic part of the susceptibility, obtained after subtracting these two contributions, is shown in Fig. 1 (curve 1) as a function of temperature. The slight increase of the susceptibility at

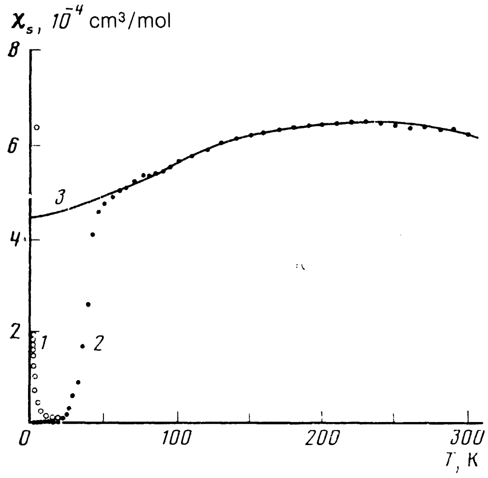

FIG. 1. Temperature dependence of the paramagnetic susceptibility: 1—total value; 2—with the paramagnetic-impurity contribution subtracted; 3—calculated using the Heisenberg one-dimensional antiferromagnetic model with $J = 170$ K.

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$T < 20$ K obeys the Curie law and can be attributed to the presence of 0.03 mol.% of localized noninteracting spins with $s = 1/2$, due to impurities or structure defects. Curve 2 of Fig. 1 corresponds to the intrinsic paramagnetic susceptibility of (BPDT–TTF)$_2$I$_3$. As seen from the figure, it is almost constant at high temperature. A gently sloping maximum is observed at $T \approx 220$ K, and with further lowering of the temperature the decrease of the susceptibility accelerates, dropping rapidly to zero at $T < 50$ K. As seen from Fig. 2, below 40 K this drop has an activation energy $\Delta = 200$ K.

The EPR measurements were performed on single crystals measuring $2 \times 0.5 \times 0.02$ mm. The EPR spectra were recorded with a standard ERS-230 homodyne spectrometer in the 3-cm band. The spectra were recorded by a computer-controlled measurement system which permitted accumulation of the signal following repeated passage through the resonance conditions, and made it also possible to determine the spin magnetic susceptibility χ_s by integrating twice the EPR spectrum. The sample temperature was set and stabilized in the EPR spectrometer with an Oxford Instruments N. A. ERS-900 flow-through cryostat capable of maintaining a temperature 3.5–300 K accurate to 0.1 K. The sample temperature was monitored with an Au-chromel thermocouple calibrated against a standard germanium thermometer. The orientation dependences of the EPR signal parameters were plotted with a goniometer accurate to 2°.

A single intense EPR signal was recorded in the entire investigated region, except at the lowest temperatures. Figures 3 shows the temperature dependence of the (peak-to-peak) EPR-signal linewidth both in the case of normal orientation of the sample plane relative to the dc field direction and for parallel orientation. In the entire temperature region, the spin susceptibility is practically equal to the static value. At $T < 50$ K the value of χ_s begins to drop abruptly (see Fig. 1). This temperature is extremal also on the $\Delta H(T)$ plot (Fig. 3)—a minimum $\Delta H = 1$ Oe is observed in the vicinity of 50 K. The g-factor also begins to increase near $T \approx 50$ K. One can deduce from the foregoing the presence of a phase transition of magnetic type at $T \approx 50$ K.

At temperatures < 20 K, where the impurity contribution becomes dominant, a certain anisotropy appears in the spin susceptibility determined by double integration of the EPR signal. This anisotropy reaches 30% at the lowest temperatures. Below 10 K there appears in the EPR spectra a doublet with a component spacing that depends on the single-crystal orientation relative to the magnetic field. The evolution of the form of the EPR spectra with change of temperature is shown in Fig. 4.

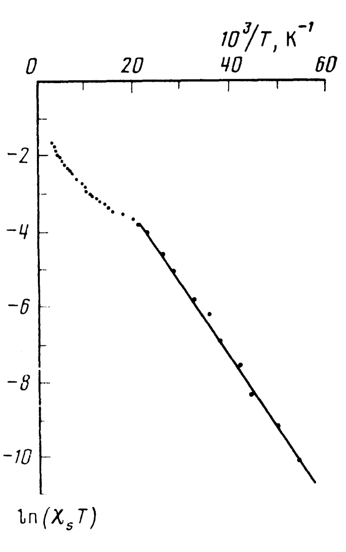

FIG. 2. Temperature dependence of the magnetic susceptibility with coordinates ln($\chi_s T$) and $1/T$. The straight line corresponds to $\Delta = 200$ K.

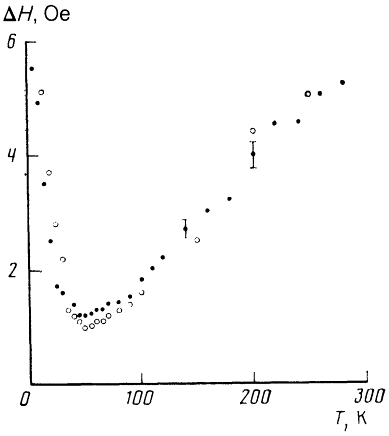

FIG. 3. Temperature dependence of the EPR linewidth (the low-temperature data correspond to the central peak); ●—$H \perp \mathbf{b}\cdot\mathbf{c}$, ○—$H \parallel \mathbf{b}\cdot\mathbf{c}$.

DISCUSSION

It is common knowledge that the presence of transitions between the nodes of the chain is equivalent, in the case of strong Coulomb repulsion, the Heisenberg exchange that leads to antiferromagnetic interactions.[7] At $T > 50$ K the paramagnetic susceptibility can be well approximated by the theoretical relation[8] for the one-dimensional isotropic model of an Heisenberg antiferromagnet with $J = 170$ K (Fig. 1). This shows that notwithstanding the general layered (two-dimensional) character of the (BPDT–TTF)$_2$I$_3$ structure the magnetic interactions are one-dimensional. A phase transition takes place at $T \approx 50$ K, due to the magnetic ordering, and is accompanied by a sharp drop of χ_s.

In principle, when the temperature is lowered a one-dimensional antiferromagnetic chain with one spin per node can undergo either a transition to a three-dimensional or-

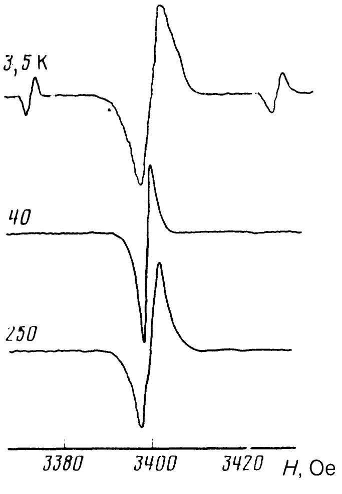

FIG. 4. Evolution of EPR spectrum with change of temperature ($H \parallel \mathbf{b}\cdot\mathbf{c}$).

dered antiferromagnetic state, or to a nonmagnetic state due to dimerization of the chain (spin-Peierls transition[9]). In either case the transition is accompanied by an abrupt drop of the susceptibility. In the case of three-dimensional antiferromagnetic ordering, however, χ_s becomes equal to zero for only one direction of the magnetic field relative to the crystal, and the averaged susceptibility is finite as $T\to 0$. In the case of a spin-Peierls transition, however, χ_s remains isotropic below T_{sp} and tends rapidly to zero when the temperature is lowered. An incontrovertible choice between these two cases can be made by analyzing the anisotropy of the EPR spectra. In the activated-decrease region χ_s is isotropic, thus excluding a treatment of the transition as three-dimensional antiferromagnetic ordering. It is curious, however, that the impurity contribution to the susceptibility χ_C, which increases in accordance with the Curie law and dominates at the lowest temperatures, exhibits a noticeable orientation dependence. A similar strong dependence of the susceptibility on the magnetic-field direction was observed also for paramagnetic impurities in La_2CuO_{4-y} single crystal.[10]

The behavior of the $(BPDT\text{–}TTF)_2I_3$ EPR spectra at low temperatures is typical for Mott insulators. For one-dimensional antiferromagnetic chains the EPR linewidth behaves like $\Delta H\propto\chi T$ (Ref. 11), in agreement with our experimental results (Fig. 3), with a linear $\Delta H(T)$ dependence above the phase-transition temperature. The observed broadening of the EPR signal in this temperature region is due to the increase of the rate of spin relaxation on ordering. At $T<20$ K the EPR signal comes from residual paramagnetic defects that are not influenced by the alternation. The spin susceptibility for these defects is $\chi C\propto 1/T$.

The decisive argument in favor of a spin-Peierls transition at $T=50$ K in $(BPDT\text{–}TTF)_2I_3$ is the observed evolution of the EPR spectra (Fig. 4). At high temperatures $T>50$ K the line shape is symmetric, as is generally typical of localized moments in paramagnetic dielectrics. At 10 K $<T<50$ K the line shape becomes asymmetric because of the inhomogeneous broadening by the magnetic ordering in $(BPDT\text{–}TTF)_2I_3$. The most interesting result is that at $T<10$ K there is observed, besides the intense resonance line from the defects (central peak in Fig. 4), a doublet whose presence can be interpreted within the framework of the classification proposed in Ref. 12. According to this reference the fine structure due to the dipole–dipole interaction between the spins can be observed at sufficiently low temperatures for the so-called Frenkel exciton (by analogy with semiconductors), which constitutes a low-lying triplet state made up of two neighboring spins. One of the main parameters of a spin-Peierls transition is the alternation parameter δ defined by the expression[9]

$$J_{1,2}=J[1\pm\delta(T)],$$

where $J_{1,2}$ are the exchange integrals after the alternation, and J is the exchange integral in the initial chain. From the fact that a Frenkel exciton has been observed it follows that the alternation parameter in $(BPDT\text{–}TTF)_2I_3$ is $\delta\approx 1$ (Ref. 12).

The observed orientational dependence of the distance δH between two fine-structure lines is described approximately by the equation for the Pake doublet[13]

$$\delta H={}^3/_2\gamma h(1-3\cos^2\theta)/r^3,$$

where γ is the gyromagnetic ratio, h is Planck's constant, θ is the angle between the radius vector joining a pair of spins and the constant magnetic field, and r is the distance between spins. From this expression we can determine the distance between the spins in a Frenkel exciton. After substituting the experimental values of δH and θ we obtain for r the value ~ 10.5 Å, which is in fair agreement with the 9.3 Å obtained from structure data,[4] thereby emphasizing the incontrovertible conclusion that a Frenkel exciton produced by two neighboring fixed spins has been observed. In addition, it follows from the form of the orientational $\delta H(\theta)$ dependence that the spins participating in the formation of a Frenkel exciton are perpendicular to the **b·c** plane.

Let us try to estimate the parameters of the spin-Peierls transition in $(BPDT\text{–}TTF)_2I_3$ from our experimental results. The transition temperature in the Hartree–Fock approximation, for the case of a weak spin–phonon interaction, is given by[9]

$$T_{sp}=2.28pJ\exp(-1/\lambda),$$

where λ is the spin–phonon interaction constant and $p\approx 1.64$ for $T_c<J$. Using the values $T_{\text{sp}}=50$ K and $J=170$ K we get $\lambda=0.39$. The alternation parameter δ is given in this approximation by $\delta(T)=\Delta(T)/pJ$, where Δ is the gap in the triplet-excitation spectrum. Substituting $\Delta(0)=200$ K in the expression for δ we get $\delta(0)=0.72$. Such large values of λ and δ agree with the picture that follows from an analysis of the EPR spectrum, and attest to the strong alternation in $(BPDT\text{–}TTF)_2I_3$ during the phase transition. The above values of λ and δ must therefore be regarded as estimates. The temperature dependence of $\Delta(T)$ in $(BPDT\text{–}TTF)_2I_3$ does not follow as BCS-type dependence, and Δ becomes constant already at $T<40$ K. At an alternation parameter $\delta\approx 1$ the spin chain can be regarded as broken up into isolated pairs. Indeed, for $T<40$ K the magnetic susceptibility of $(BPDT\text{–}TTF)_2I_3$ takes the form

$$\chi_s=N_A g^2\mu_B^2/kT(3+e^{\Delta/T}),$$

which is typical of isolated spin pairs with a gap Δ in the triplet-excitation spectrum.

It should be noted that besides the energy spin obtained in the spin-Peierls transition because of formation of a gap in the triplet-excitation spectrum, other driving forces can also lead to dimerization of a homogeneous spin chain. If the dependence of the exchange integral J on the distance between the nodes of the chain is strongly nonlinear, alternation can lead to a gain in the total exchange energy. Finally, doubling the period can be due to purely structural causes. All these factors can act simultaneously and assist the spin-Peierls transition. By measuring only the magnetic properties it is impossible to determine the true cause of the phase transition observed in $(BPDT\text{–}TTF)_2I_3$. The large alternation parameter δ for $(BPDT\text{–}TTF)_2I_3$ indicates that several factors can act here simultaneously.

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