Magnetic properties of quasi-one-dimensional organic conductor $(TSeT)_4Hg_4I_9$

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A study was made of the temperature dependence of the spin magnetic susceptibility, of the lattice-relaxation time of the ^1H nuclei, and of the ESR line profile of organic metal $(TSeT)_4Hg_4I_9$. At temperature $T < 100$ K the spin susceptibility varied in accordance with the power law $\chi_s \propto T^{-\alpha}$, where $\alpha = 0.7$, and the relaxation of the longitudinal nuclear magnetization was described by two exponential terms. An analysis of the results of measurements led to the conclusion of the existence of two inequivalent types of molecular TSeT stacks differing in their magnetic and transport properties. Stacks of one type were responsible for metallic conduction at low temperatures, whereas those of the other type cause χ_s to increase according to a power law with a fractional exponent.

Tetraselenotetracene iodomercurate $(TSeT)_4Hg_4I_9$ is an organic conductor which retains its metallic state right down to ultralow temperatures and exhibits unusual transport properties.[1] The crystal structure of this compound[2] is characterized by cation-radical molecular TSeT stacks elongated along the c axis and by continuous anion chains consisting of the Hg and I atoms. The structure includes two types of cation-radical stacks which differ slightly in the TSeT–TSeT interplanar distance and in respect of the angle between the plane of molecules and the c axis. The reasons for the absence of a metal-insulator transition in this quasi-one-dimensional conductor are not clear. It is postulated that the existence of "rigid" anion chains may give rise to the Peierls transition in the case of conducting TSeT stacks.[2] The key to the understanding of the low-temperature state of TSeT iodomercurate can be provided by information on its electron structure and magnetic properties. We obtained such information by measuring the spin magnetic susceptibility, the spin-lattice relaxation time of the ^1H nuclei, and the ESR line profile of $(TSeT)_4Hg_4I_9$ at temperatures in the range 3.5–300 K.

The results of these measurements led to the conclusion that structure-inequivalent TSeT stacks differ considerably in their magnetic and transport properties. The microscopic magnetic properties of stacks of one type are typical of the metallic state. These stacks are responsible for the retention of the high conductivity of $(TSeT)_4Hg_4I_9$ at low temperatures. Stacks of the other type exhibit behavior typical of spin chains with a random Heisenberg antiferromagnetic interaction.[3,4] This magnetic inequivalence of the stacks composed of identical molecules has not been observed before for quasi-one-dimensional organic metals.

EXPERIMENTAL METHOD

All the measurements were carried out on polycrystalline samples of $(TSeT)_4Hg_4I_9$ synthesized at the Institute of Chemical Physics of the USSR Academy of Sciences. Measurements of the spin-lattice relaxation time T_1 of the ^1H nuclei were made using a Bruker SXP 4-100 pulse NMR spectrometer at frequencies 35, 62, and 90 MHz (in fields of 8.2, 14.5, and 21.1 kOe, respectively). The values of T_1 were determined by reconstructing the amplitude of the free precession decay signal after a saturating sequence of pulses. The ESR spectra were recorded employing a standard homodyne ERS-230 spectrometer in the 3-cm range. The spectra were recorded in the digital form by employing a modular slave-master controlled by an Élektronika D3-28 computer, which made it possible to accumulate the signal data in the course of repeated passage through the resonance conditions, and also to determine the spin magnetic susceptibility χ_s by double integration of the ESR spectra.[5] The temperature of a sample was set and stabilized in both NMR and ESR experiments by Oxford Instruments CF200 and ESR900 continuous-flow helium cryostats in which temperatures could be maintained in the range 3.5–300 K to within 0.1 K. The temperature of a sample was monitored using an AuFe–Chromel thermocouple calibrated using standard platinum and germanium thermometers.

EXPERIMENTAL RESULTS

The spin magnetic susceptibility of $(TSeT)_4Hg_4I_9$ varied slightly above 100 K, but below this temperature it rose monotonically. The temperature dependence of χ_s obtained at low temperatures is shown in Fig. 1 using double logarithmic coordinates. It is clear from Fig. 1 that the low-temperature rise of χ_s can be described by a power-law dependence $\chi_s \propto T^{-\alpha}$, where $\alpha = 0.70 \pm 0.05$.

The results of measurements of the spin-lattice relaxation time of the ^1H nuclei are presented in Fig. 2. At temperatures $T < 30$ K the recovery of the longitudinal nuclear magnetization was described satisfactorily by a sum of two exponential functions corresponding to different values of T_1. The two-component recovery curve indicated the existence of two spatially separated groups of protons relaxing at different rates. The ratio of the amplitudes of these two components, representing the ratio of the numbers of protons in these groups, was close to 1:1 and did not vary with temperature. As is clear from Fig. 2, for one of these components the relaxation rate exhibited a temperature dependence of the Korringa type $[(T_1T)^{-1} = \text{const}]$ typical of ordinary metals, whereas in the case of the second component the power law $(T_1T)^{-1} \propto T^{-\beta}$, with $\beta = 150 \pm 0.04$, was obeyed.

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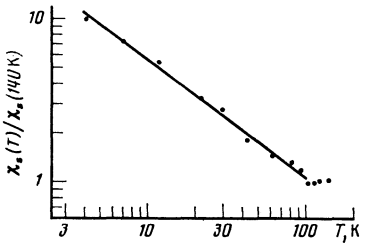

FIG. 1. Temperature dependence of the spin magnetic susceptibility of $(TSeT)_4Hg_4I_9$ measured by integration of the ESR spectrum.

For $T \approx 30$ K the recovery of the longitudinal nuclear magnetization was approximated well by a single exponential function at all the resonance frequencies. At higher temperatures $T > 30$ K the recovery curve once again could not be described by a single exponential function. However, in this temperature range the two-exponential approximation failed to provide a satisfactory description of the experimental data. The component with the longest relaxation time could be separated reliably at all temperatures. The rate of relaxation of this component was determined at various frequencies (and it is represented by appropriate symbols in Fig. 2). As is clear from Fig. 2 the temperature dependence of the relaxation rate of this component obtained in the range 30–120 K was a continuation of the low-temperature branch with $T^{-\beta}$ power-law dependence. The values of $(T_1T)^{-1}$ for the fast-relaxing components were located in the region coincided with the value of $(T_1T)^{-1}$ for the low-temperature Korringa branch. Therefore, near 30 K the temperature dependences of $(T_1T)^{-1}$ "crossed" for inequivalent proton groups. The frequency dependence of T_1 was not observed in the range 35–90 MHz.

Figure 3 shows characteristic stages of the evolution of

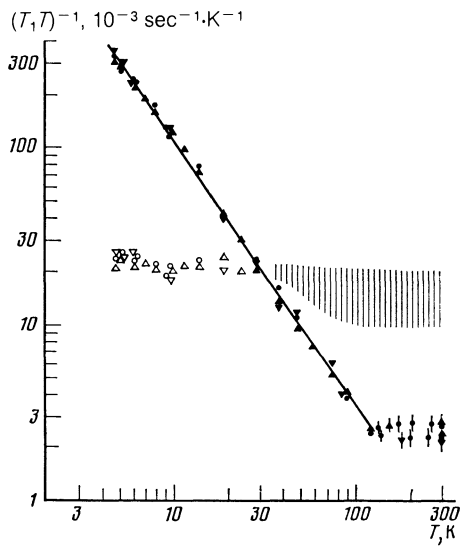

FIG. 2. Temperature dependence of $(T_1T)^{-1}$ for the ^{1}H nuclei, plotted using double logarithmic coordinates at the following frequencies: 35 MHz (▽, ▼), 62 MHz (△, ▲), 90 MHz (○, ●). The open symbols represent component I and the black symbols represent component II. The shaded region represents component I at temperatures $T > 30$ K.

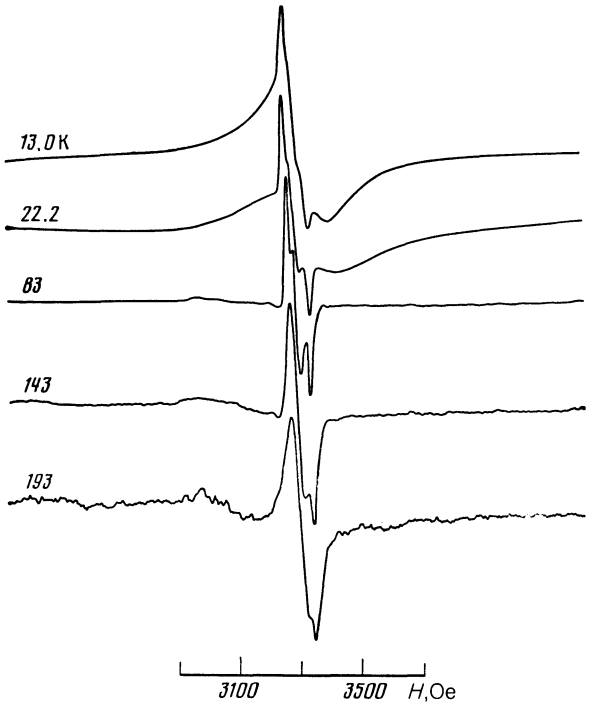

FIG. 3 Evolution of the ESR spectrum on increase in temperature.

the ESR spectrum with temperature. Throughout the investigated temperature range the ESR spectrum was a superposition of two lines. The narrower of these lines had a structure typical of the anisotropic g factor of a powder sample. The principal values of the g tensor, g_1, g_2, and g_3, obtained for this line did not vary with temperature and were 2.000 ± 0.002, 2.033 ± 0.002, and 2.050 ± 0.002, respectively. It should be noted that these values were close to the principal values of the g tensor for the $(TSeT)^+$ cation-radical.[6] Resolution of the structure of this narrow line depended on temperature because the line width for a given crystal varied with temperature. This "background" line width had its minimum near 80 K (Fig. 4). The wider line was resolved with difficulty at temperatures $T > 60$ K. At lower tempera-

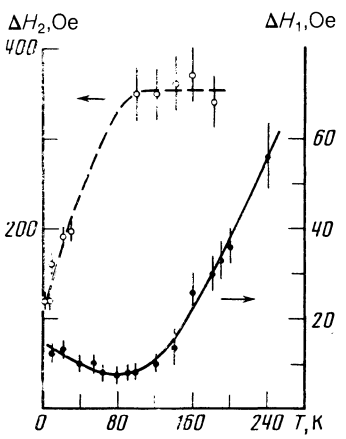

FIG. 4. Temperature dependences of the widths of the narrow (●) and wide (○) lines in the ESR spectrum.

tures the width of this line decreased (Fig. 4) and its intensity rose so that the line in question dominated the ESR spectrum and absorbed the narrow structured line. Analysis of the ESR spectra indicates that the low-temperature rise of χ_s was due to an increase in the integrated intensity of the wide line, because the intensity of the narrow line exhibited no significant changes. The low-temperature g factor of the wide line was 2.020 ± 0.005.

DISCUSSION

The low-temperature rise of the magnetic susceptibility in accordance with a power law characterized by a fractional exponent is typical of spin chains with a random Heisenberg antiferromagnetic interaction.[3,4] This behavior requires, first, a distinct one-dimensional behavior and, second, a disordered lattice.[4] According to the x-ray structure data,[1,2] the source of disorder in $(TSeT)_4Hg_4I_9$ may be the disorder of anion Hg–I chains. In the case of disordered organic conductors investigated earlier the temperature dependence of χ_s described by a fractional power law had been observed only in the region of low (semiconducting) conductivity, which agrees in principle with the model of spin chains[3,4] requiring specific localization of spins. The characteristic feature of $(TSeT)_4Hg_4I_0$ is that in this compound χ_s is observed to rise as a fractional power law in the metallic conduction region. The key to the explanation of this unusual combination of the magnetic and transport properties is provided by measurements of the nuclear spin-lattice relaxation.

The two-component restoration of the longitudinal nuclear magnetization at low temperatures when the ratio of the amplitudes of the two components is 1:1 is a direct proof of the existence of two inequivalent types of TSeT molecular stacks differing in their microscopic magnetic properties. It is natural to assume that the role of such magnetically inequivalent stacks is played by crystallographically inequivalent TSeT stacks,[1,2] the numbers of which are in the ratio 1:1. The magnetic and transport properties of $(TSeT)_4Hg_4I_9$ can then be explained qualitatively as follows. Stacks of type I retain the metallic state at low temperatures and ensure the high electrical conductivity. These stacks make only a small contribution to χ_s at low temperatures and to the Korringa component of the nuclear relaxation rate. In the case of stacks of type II the lowering of temperature results in the localization of electrons and this causes a power-law rise of χ_s and T_1^{-1}. There are also indications that charge transfer to type I stacks is considerably greater than to type II stacks.[7] Since the rise of χ_s at low temperatures is associated with an increase in the intensity of the wide ESR line, this line should be attributed to the spins in type II stacks. The narrow ESR line should be attributed to the spins in type I stacks, which is supported also by the similarity of the values of g_1, g_2, and g_3 for this line and the corresponding values for the $(TSeT)^+$ cation-radical.

The rate of the nuclear spin-lattice relaxation in a metal can be described by[8]

$$(T_1T)^{-1} = \frac{4\pi k_B}{(g\mu_B)^2\hbar}\chi_s^2 a_H^2 \langle K\rangle_F, \qquad (1)$$

where a_H is the hyperfine interaction constant, k_B is the Boltzmann constant, μ_B is the Bohr magnetron, and $\langle K\rangle_F$ is an enhancement factor averaged over the Fermi surface. For of a quasi-one-dimensional conductor, we have[9]

$$\langle K\rangle_F = {}^1/_2[K_0(\tau_c/\tau)^{1/2}G(\omega_e) + K_{2k_F}], \qquad (2)$$

where K_0 and K_{2k_F} are the static enhancement factors[8] for spin excitations with wave vectors $|\mathbf{q}| \approx 0$ and $|\mathbf{q}| \approx 2k_F$, respectively, τ is the relaxation time of the electron momentum during motion along a stack, τ_c is a cutoff parameter representing the average lifetime of electrons in one stack, and $G(\omega_e)$ is a dimensionless function of the Larmor frequency ω_e of electrons[9] with the asymptotes

$$G(\omega_e) = (2\omega_e\tau_c)^{-1/2}, \quad \omega_e\tau_c \gg 1, \qquad (3)$$

$$G(\omega_e) \approx 1, \quad \omega_e\tau_c < 1. \qquad (4)$$

We shall first consider type I stacks. The absence of the field dependence of T_1^{-1} in the range 8–21 kOe means that the condition $\omega_e\tau_c \lesssim 1$ should be satisfied throughout this range. Hence, we can estimate the upper limit to τ_c: $\tau_c \lesssim 2.6\times 10^{-12}$ sec. We can find $\langle K\rangle_F$ by substituting a_H and χ_s into Eq. (1). By way of estimate, we shall assume that the hyperfine interaction constants of protons in TSeT have the same value a_H for the $(TTT)^+$ cation-radical with a similar structure: $a_H \approx 0.6$ Oe (Ref. 6). The contribution of type I stacks to the spin susceptibility can be estimated by assuming that this contribution χ_{sI} is equal to the experimental value χ_s (300 K) $= 1.5\times 10^{-4}$ cm^3/mol (Ref. 7), i.e., that $\chi_{sII} \ll \chi_{sI}$ at 300 K, and that it is independent of temperature. The nature of the temperature dependences of $(T_1T)^{-1}$ for type I and II stacks supports the reasonable nature of this assumption (Fig. 2). We find from Eq. (1) that $\langle K\rangle_F \approx 50$. The large value of the enhancement factor shows that the experimental situation does indeed correspond to one-dimensional diffusion of the electrons limited to times exceeding τ_c.

According to Eqs. (1), (2), and (4), the absence of the temperature dependence of $(T_1T)^{-1}$ for the component I implies that the ratio τ_c/τ is independent of temperature. The parameter τ_c can be estimated from the data on the ESR line width using the Elliott formula modified to the case of quasi-one-dimensional conductors[10]:

$$\Delta H = (\Delta g)^2/\gamma_e\tau_c, \qquad (5)$$

where γ_e is the gyromagnetic ratio for the electron spin, whereas Δg is the deviation of the g factor from the value $g_0 = 2.0023$ for a free electron. If we take g to be the average of the three principal values of the g tensor for a narrow ESR line, we find from Eq. (5) that $\tau_c = 2.7\times 10^{-12}$ sec at $T = 20$ K. This result is in a reasonable agreement with an estimate τ_c obtained from the data on the nuclear relaxation rate. It should be noted that the ESR line width for type I stacks has a minimum near 80 K, i.e., the minimum occurs in the same temperature range where a minimum in electrical resistivity $\rho(T)$ is reported in Refs. 1 and 2. Moreover, at temperatures $T < 100$ K the value of ΔH_1 varies approximately proportionally to $\rho(T)$, in agreement with the fact

that the ratio τ_c/τ is independent of temperature. Therefore, interpretation of the NMR and ESR data on type I stacks does not lead to any contradictions.

An estimate of the width of the electron energy band for type I stacks from χ_{sI} carried out in the tight-binding approximation[11] gives 0.4 eV, which is half the corresponding value estimated from the thermoelectric power.[7] This may be an indication of the importance of the enhancement of χ_s by the electron-electron interaction. A similar situation occurs also in the case of organic conductors based on TMTSF (Ref. 12).

In the interpretation of the NMR data for type II stacks it is necessary to determine initially whether the electron spins responsible for nuclear relaxation are "pinned" or mobile. In the case of "pinned" spins we have $T_1^{-1} \propto \tau_e$ (Ref. 8), where τ_e is the correlation time of the electron spin. Under exchange narrowing conditions the ESR line width is $\Delta H = \langle\omega^2\rangle\tau_e/\gamma_e$, where $\langle\omega^2\rangle$ is the second moment of the ESR line system of static spins. In this case the reduction in ΔH_2 as a result of cooling should be accompanied also by a reduction in T_1^{-1} for type II stacks, which is in conflict with the experimental results. It therefore follows that the model of electron spins "pinned" to type II stacks fails to account for the nuclear relaxation rate data. In other words, the system of nuclear spins should transfer energy to the translational motion of electrons and its dynamics should be described by equations such as Eq. (1). An important piece of evidence in support of this conclusion is that, within the limits of the experimental error, the power exponent β governing the low-temperature behavior of $(T_1T)^{-1}$ is twice as large as α. This ratio follows in a natural manner from Eq. (1). Substituting in Eq. (1) the values $a_H = 0.6$ Oe and $\chi_{sII} = \chi_s - \chi_{sI}$, we find that $\langle K\rangle_F$ for type II stacks at 5 K is $\langle K\rangle_F = 60$. This value differs by only 20% from the value of $\langle K\rangle_F$ for type I stacks. Consequently, the difference between the rates of relaxation involving stacks of the two types is entirely due to the difference between the contributions of the stacks to χ_s.

The available experimental data are in sufficient to draw the final conclusion on the nature of the interacting electron spins in type II stacks. Bearing in mind an analysis of the various possible models given in Ref. 13 and the nuclear relaxation data, preference should be given to the description of type II stacks within the framework of the model of localization of weakly interacting electrons because of disorder.[14] A theoretical description suitable for the analysis of the width of the ESR line of type II stacks is not yet available because the dynamics of a one-dimensional spin system with a random interaction is complicated. We can simply note that the reduction in ΔH_2 we have observed at low temperatures is typical of many disordered organic conductors.[15]

It therefore follows that the results of an investigation of the magnetic properties of $(TSeT)_4Hg_4I_9$ by local methods are a demonstration of the magnetic inequivalence of cation stacks. The existence of such inequivalent stacks makes it possible to explain qualitatively the unusual combination of the transport and magnetic properties of this compound at low temperatures. The problem of the nature of spins responsible for the rise of the magnetic susceptibility in accordance with a fractional-exponent power law requires further study.

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