

## Spin Relaxation Studies on Conducting Poly(Tetrathiafulvalene)

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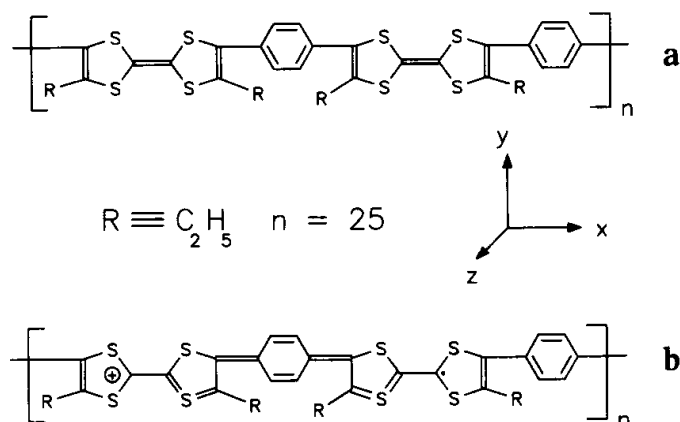
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**Abstract.** Magnetic parameters and the relaxation behavior of paramagnetic centers in an iodine-doped poly(tetrathiafulvalene) semiconductor with a d.c. conductivity of  $10^{-5} \text{ S} \cdot \text{cm}^{-1}$  have been studied using mainly the 2 mm waveband EPR technique in the temperature range of 110–270 K. The EPR line shape analysis confirms the existence of immobile radicals pinned on short polymer chains and mobile polarons with different relaxation parameters in slightly doped poly(tetrathiafulvalene). The temperature dependences of electron spin-lattice and spin-spin relaxation times of paramagnetic centers of both types have been determined independently using the saturation method at the operation frequency  $\nu_e = 140 \text{ GHz}$ . An anisotropic slow libration of immobile polarons with an activation energy of 0.02 eV have been registered for the first time using the saturation transfer EPR method. The temperature dependences of intrachain diffusion and interchain hopping rates in poly(tetrathiafulvalene) are determined from the  $T_1$  and  $T_2$  EPR data. The interchain spin dynamics is shown to correlate with libration of polarons trapped on polymer chains and is in good agreement with a hopping charge transport mechanism.

### 1. Introduction

The doping-induced charge formation in conjugated polymers of the poly(p-phenylene) type are usually discussed in terms of polaron/bipolaron concepts [1, 2]. According to a single-particle theory, both types of topological defects are associated with two localized levels positioned symmetrically near the mid-gap. The polaron state is characterized by a  $\pm e$  charge and a spin  $S = 1/2$ . Since the polaron has an unpaired electron, the spin dynamics can be studied using electron paramagnetic resonance (EPR) and electron spin echo (ESE) techniques [3]. Such investigations are usually carried out at 3 cm waveband. However, at this band the EPR spectra of organic free radicals are registered in a narrow range of the magnetic field where the exchange rate between separate spin packets is high in comparison with its width and the overlapping effect exists. It causes a low spectral resolution of



**Fig. 1.** The molecular structure of the initial PTTF sample (a) and the polaron formed in its chain due to doping by iodine vapor (b). The length and the charge of the polaron are in fact spread out to a larger extent than shown here.

complicated EPR spectra of different paramagnetic centers (PCs) and renders more difficult the investigation of polymer semiconductors.

Poly(tetrathiafulvalene) (PTTF) (Fig. 1a) is a convenient polymer semiconductor for the study of fundamental dynamic processes which take place in conjugated compounds. Various PTTF samples were investigated earlier [4, 5] using 3 cm waveband EPR and ESE magnetic resonance methods. It has been shown [5], that the EPR spectrum of doped PTTF is a superposition of lines attributed to immobile PCs with an anisotropic  $g$ -tensor and to the mobile centers possessing a singlet EPR line, the concentration ratio of these PCs being less than 1 : 10. However, the low spectral resolution at this waveband did not permit a complete investigation of the nature, composition and dynamics of PCs in PTTF.

As shown in our previous papers [6–10], at 2 mm waveband the spectral resolution and information is increased considerably and more complete investigations of the structure and dynamic properties of PCs in conjugated polymers are possible.

In the present work both high spectral resolution and saturation effects at 2 mm wave band EPR have been used for a more complete determination of the nature and dynamics of trapped and mobile PCs in a slightly doped PTTF sample. Moreover, we have demonstrated the possibility of studying superslow anisotropic molecular reorientations in conjugated polymers using 2 mm waveband saturation transfer EPR (ST EPR).

## 2. Experimental

EPR experiments were performed using 3 cm (PS 100.X), 8 mm (RE-1308) waveband EPR spectrometers and a 2 mm (EPR5-01) spectrometer with a

superconductive magnet described in detail in [11]. The setting of the microwave field and the a.c. modulation phases was made on a  $(\text{DBTTF})_3\text{PtBr}_6$  single crystal as an external standard (see [8]). This standard was also used to measure the PC concentration. Another standard,  $\text{Mn}^{2+}$  with  $g_{\text{eff}} = 2.00102$  and  $a = 87.4$  G, was used for the determination of the  $g$ -factor as well as for the magnetic field sweep scale calibration at the 2 mm waveband. EPR spectra were recorded for both imaginary and real parts of the paramagnetic susceptibility.

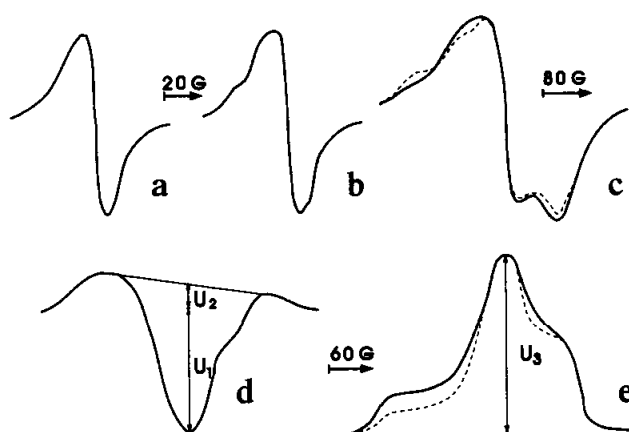
The powder-like PTF sample (doping level of  $y = 0.4$ , d.c. conductivity of  $10^{-5} \text{ S} \cdot \text{cm}^{-1}$  and total spin concentration of  $1 \cdot 10^{18} \text{ spin/cm}^3$ ) synthesized according to [12] was placed into a quartz capillary with an external diameter of 0.5 mm and length of 5 mm. However, the real measured length of the sample was about 1.5 mm.

### 3. Results and Discussion

#### 3.1. Nature and Composition of PCs in the PTF

At the 3 cm waveband the PTF sample demonstrates a total nearly symmetrical signal with a weak spectrum of immobilized PCs overlapping (Fig. 2a). At the 8 mm waveband this signal somewhat broadens and individual components of immobilized PCs are manifested more evidently (Fig. 2b).

The 2 mm waveband EPR absorption spectra of the sample are more informative (Fig. 2c). They allow a determination of the major components of the



**Fig. 2.** The EPR in-phase absorption spectra registered at 3 cm (a), 8 mm (b) and 2 mm (c) wavebands and the 2 mm waveband in-phase (d) and  $\pi/2$ -out-of-phase (e) dispersion spectra of slightly doped PTF sample. The simulated (c) and registered at 110 K (e) EPR spectra are shown by dotted line.

anisotropic  $g$ -tensor and the separation of lines of different shapes. Computer simulation shows that the signal is a superposition of a strongly asymmetric spectrum with temperature independent magnetic parameters of  $g_x = 2.01424$ ,  $g_y = 2.00651$ ,  $g_z = 2.00235$  and a symmetric one with  $g_p = 2.00706$ . PCs of different types are present in the sample with a concentration ratio of 1 : 1.8, or  $n_1 = 3.8 \cdot 10^{-5}$  and  $n_2 = 6.9 \cdot 10^{-5}$  spin per monomer unit, respectively, in the low temperature region.

The  $g_p$  value is close to the average  $g$ -factor of the immobile PCs determined as  $\langle g \rangle = 1/3(g_x + g_y + g_z) = 2.00770$ . We have shown previously [6, 8, 9] that the principal components of the  $g$ -tensor of PCs in some conjugated polymers could be averaged due to PCs moving at the rate  $\nu_{1D}^0 \geq (g_x - g_z)\beta H_0/\hbar$  [13]. So PCs of two types with approximately equal magnetic parameters exist in PTTF; these are polarons moving along the polymer  $X$ -axis with a rate of  $\nu_{1D}^0 \geq 5 \cdot 10^9 \text{ s}^{-1}$  and polarons pinned on the short polymer chain segments (Fig. 1b). The amount of mobile polarons increases with the dopant concentration [4], due to chemical reaction and increasing mobility of the polymer matrix because of softening by large iodine ions.

The linewidth of the EPR spectral components of immobile polarons,  $\Delta H_{pp}^{imm}$ , is temperature-independent and may vary within 2.8–3.8 and then to 39 G when the operation microwave frequency  $\nu_e$  increases from 9.5 to 37 and then to 140 GHz, respectively. The linewidth of mobile polarons,  $\Delta H_{pp}^{mob}$ , in this case increases at 270 K from 10 to 11.2 and then to 175 G, respectively. Note, that whereas the spectral width of some conductive polymers increases nearly quadratically in the whole range of  $9.5 \text{ GHz} \leq \nu_e \leq 140 \text{ GHz}$  [6, 8, 9], the linewidth of both types of PCs in PTTF increases quadratically only in the  $37 \text{ GHz} \leq \nu_e \leq 140 \text{ GHz}$  frequency region. This will be discussed in terms of non-interacting spin-packets in the next Section. The fact that mobile PCs have a broader line than the immobile ones may be explained by the strong interaction with dopants as shown in [14] for various dopants. So the mobile PCs have probably a stronger interaction with the dopants than the immobile PCs. This is not in agreement with the interpretation given in [5].

The decrease in the spectral linewidth of the mobile polarons by 22 G together with a 2-fold temperature decrease indicates that the mobility of the polarons increases as the temperature falls and that so-called motional narrowing of the line takes place. Such a change in  $\Delta H_{pp}^{mob}$  is very similar to the temperature dependence of the linewidth in metals.

### 3.2. Passage Effects in EPR Spectra of the PTTF

Spin-packets in paramagnetic systems are characterized by spin-lattice  $T_1$ , spin-spin  $T_2$  relaxation times, resonance frequencies  $\omega_i$  and exchange fre-

quency  $\nu_{\text{ex}}$ . In a reasonably strong magnetic field the  $\nu_{\text{ex}}$  value decreases considerably, so that the line broadens inhomogeneously with a total width of  $\Delta H_{\text{pp}} = 1/(\gamma_e T_2) + \Delta\omega_{ij}^2/(8\gamma_e \nu_{\text{ex}})$  [15] and is described by the Gaussian distribution function of separate non-interacting spin-packets. The passage effects are observed in the EPR spectrum under the condition for microwave saturation of spin-packets:

$$\gamma_e H_1 \sqrt{T_1 T_2} > 1, \quad (1)$$

and the well-known conditions of adiabatic resonance passage:

$$\frac{dH}{dt} = H_m \omega_m < \gamma_e H_1^2, \quad (2a)$$

$$\gamma_e H_m \ll \Delta\omega_G, \quad (2b)$$

$$\omega_m T_1 \leq 1, \quad (2c)$$

where  $\gamma_e$  is the gyromagnetic ratio for electron,  $dH/dt$  is the rate of resonance passage,  $H_m$  and  $\omega_m$  are the a.c. modulation amplitude and angular frequency, respectively and  $\Delta\omega_G$  is the width of a Gaussian spin-packet distribution. In this case the precession period of the magnetization vector  $\mathbf{M}$  of PCs around the vector  $\mathbf{H}_1$  becomes smaller than the effective electron relaxation time  $T_{\text{eff}} = \sqrt{T_1 T_2}$  and as a result the relaxation processes within the resonance conditions do not produce a strong effect on the behavior of the  $\mathbf{M}$  rotation. So the first derivative of the dispersion signal  $U$  during resonance passage of the spins associated contains the in-phase,  $\pi$ -out-of-phase and  $\pi/2$ -out-of-phase components [16]:

$$U = U_1 \sin(\omega_m t) + U_2 \sin(\omega_m t - \pi) + U_3 \sin\left(\omega_m t - \frac{\pi}{2}\right), \quad (3)$$

The components of the dispersion signal  $U$  can be registered separately using a proper phase adjustment in the phase-look detector.

Since the linewidth of both types of PCs in PTTF increases quadratically with an increase in  $\nu_e$  from 37 to 140 GHz, the  $\nu_{\text{ex}}$  value decreases at  $\nu_e \geq 37$  GHz and spin-packet interaction appears to be inhibited. The  $\pi$ - and  $\pi/2$ -out-of-phase components of the dispersion signal are registered at the 2 mm waveband EPR, as conditions Eq.(1) and Eq.(2) hold (Figs. 2d and 2e). The  $\omega_m T_1 \leq 1$  inequality is realized for this sample, so that the first derivative of its dispersion signal is mainly determined by the  $U_1$  and  $U_3$  terms of Eq.(3). This passage effect may be used to determine the relaxation parameters of PCs in PTTF as shown in [8–10, 17, 18].

The simulation of the spectra in Figs. 2d and 2e has shown that there is a superposition of a predominant asymmetric spectrum with  $g_x = 2.01356$ ,  $g_y = 2.00603$ ,  $g_z = 2.00215$ ,  $\Delta H_{PP}^{imm} = 38$  G and a symmetric spectrum with  $g_{AV} = 2.00710$ ,  $\Delta H_{PP}^{mob} = 170$  G at 230 K which are attributed to immobile and mobile polarons, respectively. The components  $U_i^X$ ,  $U_i^Y$ ,  $U_i^Z$  of the dispersion signal  $U$  corresponding to the parts of a strong asymmetric spectrum are caused by the principal values of the  $g$ -tensor. In a symmetric spectrum these components are averaged. The relaxation times of different type PCs can be determined separately from their contribution to the  $\pi$ - and  $\pi/2$ -out-of-phase dispersion signals. Fig. 3 gives  $T_1$  and  $T_2$  of both types of PCs in the PTFE sample *versus* temperature determined from 2 mm EPR spectra registered under conditions Eq.(1) and Eq.(2). Thus  $T_1$  changes with temperature like  $T^{-\alpha}$ , where  $\alpha = 3.3$  and  $3.7$  for localized and mobile polarons, respectively. The exponent  $\alpha$  determined from the 2 mm waveband EPR is larger than that measured for immobile radicals using 3 cm ESE [5]. This deviation may be explained by the circumstance, that at 2 mm waveband a lot of radicals appear as immobile PCs which at 3 cm waveband are counted as mobile ones (because of the lower measuring frequency). For that reason also the absolute values of relaxation times are somewhat shorter at the 2 mm waveband compared with that measured for the immobile radicals at the 3 cm waveband [5]. However, other explanations of such relaxation times shortening may be also proposed. The small difference between  $T_1^{mob}$  and  $T_1^{imm}$  may be a hint on a strong interaction and energy exchange between mobile and immobile PCs.

The spin-lattice relaxation time  $T_1$  in conjugated polymers behaves usually like  $T^{-2}$  at temperatures above 20 K [8, 9, 19, 20]. Such behavior at relatively high temperatures is explained by a Raman relaxation process in which two lattice phonons are involved. Our results are not relevant to the existing theory based on harmonic lattice motion.

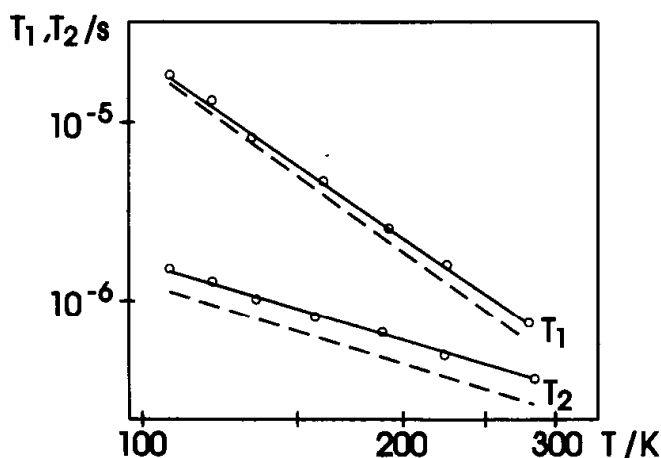


Fig. 3. The temperature dependences of electron spin-lattice and spin-spin relaxation times of immobile (solid lines) and of mobile polarons (dotted lines) in PTFE sample.

### 3.3. Microwave Saturation Transfer in the PTF Spectrum

The motion of chains in conjugated polymers, similarly to ordinary ones, is *a priori* strongly anisotropic with a correlation time  $\tau_c \geq 10^{-7}$  s. The widely used, "linear" EPR method in which the in-phase absorption signal is registered is not sensitive to such molecular processes. In this case the microwave saturation transfer EPR (ST EPR) method based on the saturation effect can be used [21].

According to the ST EPR approach, if conditions Eq.(1) and Eq.(2) hold, the chain reorientation causes spins to pass through the resonance condition because of the anisotropy of the magnetic interaction, and the last two terms in Eq.(3) become sensitive to the electron relaxation and dynamical processes. If a slow molecular motion around, e.g., the *X*-axis occurs, the inequality Eq.(1) may be not satisfied for radicals oriented with their *Y*- or *Z*-axis parallel to the direction of the external magnetic field. The spectral diffusion of microwave saturation across the spectrum occurs and the intensity of the *Y* and *Z* spectral components decreases. To find the preferable axis of a slow reorientation of macromolecules it is therefore necessary to register all principal ST EPR spectral components.

We showed earlier [17, 18] that the sensitivity of the ST EPR method to very slow molecular motion increases at the 2 mm waveband, which makes it possible to determine the relaxation and anisotropic motional processes separately.

PCs trapped in PTF are themselves sensors of polymer properties. As the sensitivity of the ST EPR method to molecular motion is enhanced quadratically with the magnitude of the anisotropy of the magnetic interaction [21], one hopes that the 2 mm waveband ST EPR method will be effective for the investigation of PTF immobilized PCs with a strongly anisotropic *g*-tensor.

Calculations made for small angle radical hopping [17] have shown that for these PCs the  $K_{rel} = U_3^Y/U_1^Y$  and  $K_{mov} = U_3^X/U_3^Y$  values are sensitive to spin relaxation and motional processes, respectively. The former ratio has been used to determine the relaxation parameters of PTF.

The  $K_{mov} = U_3^X/U_3^Y$  ratio increases with temperature (Fig. 2e). This fact can be unambiguously attributed to very slow anisotropic librational reorientations of the immobile PCs near the *X*-axis of the polymer chains. The correlation time of such libration determined from the PTF ST EPR spectra using the method described in [17, 18] follows the  $\tau_c = 9.8 \cdot 10^{-6} \exp(0.02 \text{ eV}/kT)$  law (Fig. 4). When either  $\tau_c$  grows or  $H_1$  decreases considerably the saturation transfer effect is not observed and  $K_{mov}$  reaches the value of 0.07. Extrapolation of the plot shown in Fig. 4 to lower temperatures gives a value of  $\tau_c \approx 10^{-4}$  s if  $K_{mov} = 0.07$  (75 K). This is just the maximum registerable  $\tau_c$  value for PTF sample by the 2 mm waveband ST EPR method. It should be noted that the activation energy of such librations is comparable with that of

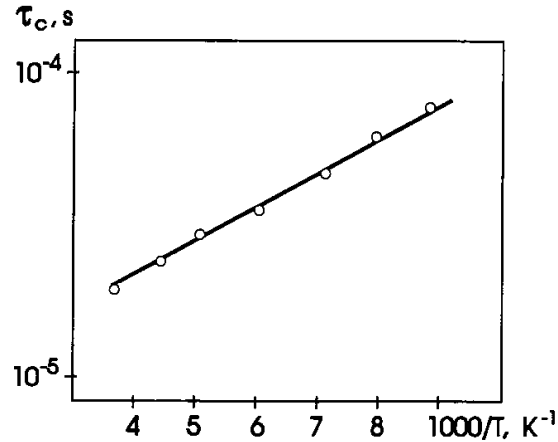


Fig. 4. The correlation time of the  $X$ -anisotropic libration of PTF chains *versus* temperature.

d.c. conductivity of a lightly doped PTF sample [5], which indicates the interaction of pinned and mobile polarons in PTF.

### 3.4. 1D Spin Dynamics in PTF

Although the PTF is considerably more complex chemically, a number of analogies can be drawn between their electronic transport properties and those of other conjugated poly(*p*-phenylene)-like semiconductors.

In order to compare our experimental results with polaron theory, we assume the in-chain quasi-one-dimensional (1D) diffusive motion of mobile PCs in PTF with a rate of  $\nu_{1D}$  and three-dimensional (3D) hopping between the chains with a frequency of  $\nu_{3D}$ . In this case one gets the following Fourier fluctuation power spectrum [22]:

$$\varphi(\nu) = (4\pi\nu'_{1D}\nu_e)^{-0.5}, \quad \text{if } \nu'_{1D} \gg \nu_e \gg \nu_{3D}, \quad (4a)$$

$$\varphi(\nu) = (4\pi\nu_{3D}\nu_e)^{-0.5}, \quad \text{if } \nu'_{1D} \gg \nu_{3D} \gg \nu_e, \quad (4b)$$

and the spectral density

$$J(\nu) = n\varphi(\nu)\Sigma_{ij} \quad (5)$$

of 1D electron spin motion, where  $n = n_1 + n_2/\sqrt{2}$  is the total PC concentration per PTF monomer,  $\Sigma_{ij}$  is the powder averaged lattice sum. Assuming that the electron relaxation is determined mainly by dipole-dipole interaction between spins, one can write the expressions for such rates [23]:



$$T_1^{-1} = \langle \omega^2 \rangle [\varphi_1(\nu_e) + 4\varphi_2(2\nu_e)] , \quad (6a)$$

$$T_2^{-1} = \frac{\langle \omega^2 \rangle}{2} [3\varphi_0(0) + 5\varphi_1(\nu_e) + 2\varphi_2(2\nu_e)] , \quad (6b)$$

where  $\langle \omega^2 \rangle = 1/5(\mu_0/4\pi)^2 \gamma_e^4 \hbar^2 S(S+1)n\Sigma_{ij}$  is the second momentum of the spectral line.

The temperature dependences of  $\nu'_{1D}$  and  $\nu_{3D}$  calculated using Eqs.(6) and data presented in Fig. 3 are shown in Fig. 5. Extrapolation to room temperature displays that the maximum value of  $\nu'_{1D}$  of PTF sample does not exceed  $5 \cdot 10^9 \text{ s}^{-1}$ . If one takes into account the fact that the spin delocalization over the polaron in conjugated polymers occupies approximately from three to five monomer units [24], then  $\nu_{1D} \leq 2 \cdot 10^{10} \text{ s}^{-1}$  is correct. This value is at least two orders of magnitude lower than that determined from magnetic resonance measurements for polarons in polypyrrole [25] and polyaniline [26]. However, there is the 1D spin motion with anisotropy of  $\nu_{1D}/\nu_{3D} \geq 8$  and rate higher than  $\nu_{1D}^0$  in PTF.

The spin dynamical behavior can be related to the charge transport properties. At equal diffusion coefficients for both spin and charge carriers, the PTF's on-chain and interchain conductivities can be estimated from  $\nu_{1D}$  and  $\nu_{3D}$  using the Einstein relation:

$$\sigma_{1D,3D} = n_2 e^2 \nu_{1D,3D} \frac{d^2}{kT} , \quad (7)$$

where  $d$  is the lattice constant and  $k$  is the Boltzmann constant. With  $n_2 = 6.9 \cdot 10^{-5} \bar{e}$  per monomer, one obtains values of  $\sigma_{1D} \cong 1 \cdot 10^{-3}$  and  $\sigma_{3D} \cong 4 \cdot 10^{-5} \text{ S/cm}$  for the intrinsic inchain and interchain conductivities,

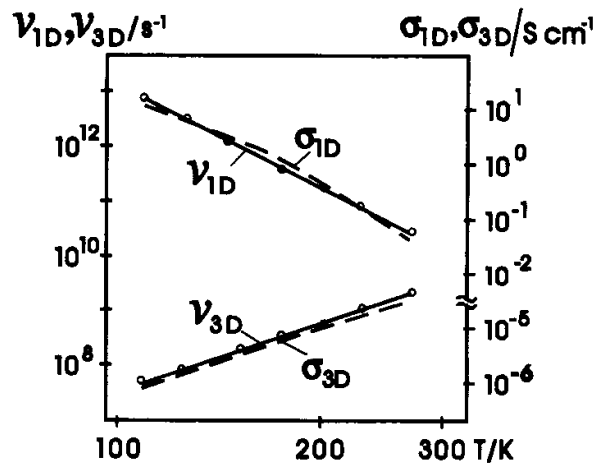


Fig. 5. The temperature dependences of the on-chain diffusion  $\nu'_{1D}$ , interchain hopping  $\nu_{3D}$  rates and a.c. ( $\nu_e = 140 \text{ GHz}$ ) conductivities of the PTF calculated using the relations  $\sigma_{1D}(T) = K'\nu_e T^{-1}[\ln(K_1 \nu_e T^{-n-1})]^4$  and  $\sigma_{3D} = \sigma_0 \nu^3 T \exp(-E_a'/kT)$  (see the text).

respectively, in the room temperature region. The former value is at least two orders of magnitude larger than  $\sigma_{dc} \approx 10^{-5}$  S/cm for PTFE. In fact, the electrical conductivity, which is a macroscopic value, is limited by hopping processes between polymer segments, while the microscopic conductivity which is probed by the EPR method is higher. Taking into account the difference in temperature behavior of  $\sigma_{1D}$  and  $\sigma_{3D}$  [27],  $\sigma_{dc}$  and  $\sigma_{ac}$  [28] of conjugated polymers one can suggest the following possible mechanisms of charge transport in PTFE.

One of the mechanisms can be described in terms of Kivelson's theory of electrical conduction in lightly doped polyacetylene [29], who considered phonon-assisted hopping between gap states applied to charged-neutral soliton pairs in  $(CH)_x$  chains. In PTFE the  $\nu'_{1D}(T)$  dependence was shown (see Fig. 5) to be in good agreement with  $\sigma_{1D}(T)$  calculated using Eq.(7) and  $\sigma_{1D}(T) = K' \nu_e T^{-1} [\ln(K_1 \nu_e T^{-n-1})]^4$  ( $K' = 1.7 \cdot 10^{-13}$  S·s·K/cm,  $K_1 = 1 \cdot 10^{24}$  s·K $^{n+1}$ ,  $n = 12.6$ ) which follows from Kivelson's isoenergetic interchain electron hopping formalism. This charge transport mechanism should lead to a strong temperature dependence of the nonactivated  $\sigma_{dc}(T) \propto T^{12.6}$  value, as is observed in the case of *trans*-(CH) $_x$  [28]. However, the experimentally obtained  $\sigma_{3D}(T)$  is changed by a factor of only  $\sim 30$  for a two times increase in temperature and  $\sigma_{dc}(T)$  of PTFE is proportional to  $\exp(-E_a/kT)$  [5], i.e. it is of an activation character. The most acceptable spin dynamical process is therefore a thermally activated polaron hopping in conduction band tails [30]. In this case the temperature dependence of the a.c. and d.c. conductivity is determined mainly by the number of charge carriers excited to the band tails. Thus  $\sigma_{dc} = \sigma_0 \exp(-E'_a/kT)$  and  $\sigma_{ac} = \sigma'_0 \nu^s T \exp(-E'_a/kT)$  with  $E'_a < E_a$ . Here  $E_a$  is the energy for activation to extended states.

As is seen in Fig. 5, the temperature dependence of  $\nu_{3D}$  of PTFE approximately follows the  $\sigma_{ac} = \sigma'_0 \nu^s T \exp(-E'_a/kT)$  conductivity law of the temperature activated polaron hopping formalism if  $\sigma'_0 = 8.3 \cdot 10^{-16}$  S·s/cm·K,  $\nu_e = 1.4 \cdot 10^{11}$  Hz,  $s = 0.8$  [28] and  $E'_a = 0.04$  eV. The obtained activation energy is of the same order of magnitude as  $E_a = 0.03$  eV of the  $\sigma_{dc}$  change in the low temperature region [5]. Besides, this value is close to  $E_a = 0.03$  eV [27] of doped polyaniline for both  $\sigma_{ac}$  and  $\sigma_{dc}$  which are dominated by interchain spin hopping. Finally, the  $E'_a$  value corresponds to the activation energy for PTFE chain libration,  $E_a = 0.02$  eV. These facts lead to the conclusion that the conductivity of PTFE is determined mainly by polaron interchain phonon-assisted hopping.

The charge transport depends upon the strength of the electron-lattice interaction. A jump generally occurs with absorption of more than the minimum number of phonons  $m$  required by the energy conservation law. As shown in Fig. 4, the interchain hopping rate increases with temperature and may be approximated by the power law  $\nu_{3D} \propto T^{4.7}$ . On the other hand, the spin-lattice relaxation rate of PCs reflected multiphonon process in PTFE has a  $T^{3.6}$

dependence (see Fig. 3). Thus, using the averaged  $m = 4.2$  and the relation  $E'_a = m h \nu_{\text{ph}}$ , the frequency  $\nu_{\text{ph}} = 2.5 \cdot 10^{13} \text{ s}^{-1}$  for phonons in PTFE can be determined. The sample conductivity is stimulated by multiphonon processes and is determined by the heat libration of polymer chains due to strong electron-lattice coupling.

The behavior of  $\sigma_{1D}(T)$  and of  $\Delta H_{\text{PP}}^{\text{mob}}(T)$  dependences suggests a metallic state for PTFE. However, from the room-temperature data one can estimate the charge-carrier mean free path  $l^*$  with the assumption of metallic behavior from  $\nu_{\parallel} d_{\parallel}^2 = \nu_{\text{F}} l^*$ , where  $d_{\parallel} = 1.17 \text{ nm}$  is the cell constant and  $\nu_{\text{F}}$  is the Fermi velocity. One obtains  $l^*/d_{\parallel} \cong 2 \cdot 10^{-4}$ , which is much too small a value to be consistent with a metallic description proposed in [31].

#### 4. Conclusions

The results show that both diffusive in-chain and hopping interchain spin dynamical processes occur in PTFE, but the conductivity is shown to be dominated by the latter mechanism. However, a 1D spin diffusive motion should not be completely neglected for the charge dynamical properties of PTFE and other conductive polymers. If a small number ( $\sim 5\%$ ) of mobile PCs play an auxiliary role in *trans*-(CH)<sub>x</sub> to facilitate intersoliton electron transport [7], the interchain polaron motion is responsible for the electrical conductivity in PTFE. Thus the separate determination of both 1D and 3D spin dynamics is necessary for every polymer. Such a possibility can be achieved by spin dynamical studies of different conjugated polymers using the 2 mm waveband EPR technique.

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