

Electron-spin dynamics of polarons in lightly doped polypyrroles

Katsuichi Kanemoto and Jun Yamauchi

Graduate School of Human and Environmental Studies, Kyoto University, Kyoto 606-8501, Japan

(Received 21 April 1999; revised manuscript received 5 August 1999)

This paper examines the spin dynamics of polarons in lightly doped polypyrrole (PPy), on the basis of the temperature dependence of spin-relaxation rates determined by a pulsed ESR technique. Several experiments using pulse equipment indicate that observed spins are averaged out over several levels and that one spin species is detected, while the susceptibility suggests the coexistence of Pauli and Curie types of spins. We consider that the discrepancy originates from a rapid motion of the spins distributing over possible levels. The spin-relaxation rates scarcely changed for a variety of dopants, but we observed remarkable decreases resulting from the deuteration of PPy in T_1^{-1} as well as T_2^{-1} . Two models, the quasi-one-dimensional (Q1D) diffusion model and the random diffusion model, indicate that observed spins diffuse quasi-three-dimensionally. We point out that the Q1D diffusion model is not necessarily desirable for such a less anisotropic motion. In contrast, the random diffusion model supposing an exponential type of correlation function can successfully interpret the decreases resulting from the deuteration in T_1^{-1} and T_2^{-1} as attributed to the difference in local fields (hyperfine field), independently of the temperature. We emphasize that the spin-correlation rate deduced from the latter model gives an estimate of the hopping rate of polarons in lightly doped PPy.

I. INTRODUCTION

For almost two decades, conjugated polymers containing paramagnetic spins have been fascinating subjects of ESR research, and many studies using ESR techniques have been devoted to characterizing those physical properties. Yet, significant information on pinning states, such as the anisotropies of a g factor and a hyperfine-coupling constant, has hardly ever been obtained because of the high mobility of the electrons spins. Among those polymers, *trans*-polyacetylene (*t*-PA), the first reported on the presence of paramagnetic defects,¹ has been paid the most attention. The paramagnetic spins were interpreted theoretically in terms of the soliton model,² on the basis of which a proof of the fast spin diffusion has been experimentally provided.³ Since then, numerous experimental techniques of magnetic resonance spectroscopies have been applied in order to investigate the soliton dynamics, as summarized in Refs. 4 and 5. Especially, on the quantitative study of the spin dynamics of neutral solitons, both the temperature and the frequency dependences of proton spin-relaxation rate⁶⁻⁸ and ESR linewidth^{7,9} have played important roles. Although there were several controversies over the interpretation of the data, some features have been drawn: the neutral solitons diffuse via quasi-one-dimensional motion, and two types of solitons exist, diffusing and trapped ones.

In many conducting polymers, charged solitons, polarons, and bipolarons have been considered to be the species responsible for conductivity. Especially, recent reports on heavily doped polypyrrole (PPy), pointed out the possibility of polarons working as conductive carriers, *via* observing the magnetoresistance¹⁰ and the Pauli susceptibility.¹¹⁻¹³ Yet, in examining the spin dynamics of the polarons, the coexistence of polarons and solitons occurring in *t*-PA is undesirable because of the difficulty involved in distinguishing those spin motions. In this sense, PPy, with nondegenerate ground states, is one of the most appropriate polymers to avoid such a coexistence.

So far, several techniques of magnetic resonance have

been applied to PPy in the heavy doped region, and then the several features of the polarons have been reported; the dimensionality of the motion was suggested to increase with the rise of temperature by a NMR technique,¹⁴ and the linewidth in ESR was shown to exhibit the Elliott-type behavior¹⁵ typical of electron spins in metallic conductors.¹⁶ In contrast, recently, we pointed out that there is a distinct difference in spin-relaxation behaviors of PPy depending on the doping level; in lightly doped PPy, the Elliott-like contribution seems to be absent.¹⁷ Thus, the polarons dynamics is suggested to vary depending on the doping level.

In this paper, the spin dynamics of polarons in the lightly doped PPy is examined in detail, especially on the basis of temperature dependences in relaxation rates T_1^{-1} as well as T_2^{-1} determined by a pulsed ESR technique. Such a technique is appreciably powerful because it gives significant information on the inhomogeneity around spins and enables the intrinsic observation of spin relaxation. Here, we attach great importance to the comparisons of spin relaxation rates between isotope-labeled samples. A similar comparison was made in *t*-PA to the deuterated one,¹⁸⁻²⁰ and the contribution of proton-hyperfine coupling to the relaxation rates was ascertained.^{18,19} In our samples, we reveal that the influence of hyperfine interaction, more remarkable than in *t*-PA, plays important roles in exploring the spin dynamics.

II. EXPERIMENTAL

Several types of samples were electrochemically synthesized at room temperature in a glove box under Ar atmosphere. Preparing conditions (monomers, dopant anions, potential values and solvents) are listed in Table I. Isotope-labeled agents employed were D₂O 99.9% (EURISO-TOP), pyrrole-*d*₅ 98% (ALDRICH) and NaNO₃-¹⁵N 98% (ALDRICH). As a typical case, C-1 was synthesized in H₂O containing 0.2 M pyrrole monomer and 0.05 M LiClO₄. ITO glass and platinum were used as working and counter elec-

TABLE I. Preparing condition for all the samples.

Sample	Monomer	Dopant anion	Potential (mV)	Solvent
C-1	Pyrrole	ClO_4^-	-0.80	H_2O
C-2	Pyrrole	ClO_4^-	-0.65	H_2O
D	Pyrrole- d_5	ClO_4^-	-0.80	D_2O
N-1	Pyrrole	$^{14}\text{NO}_3^-$	-0.80	H_2O
N-2	Pyrrole	$^{15}\text{NO}_3^-$	-0.80	H_2O

trodes, respectively. An Ag/AgCl electrode was employed as a reference electrode. All the samples were prepared from an electrochemical reduction of the oxidized films produced on the anode electrode and characterized by their potential values for the references. Dopant concentrations of C-1 and N-1 were determined to be 9.7 and 7.2%, respectively, from elemental analyses.

All the samples were sealed under vacuum into quartz ESR tubes without any contact to air in order to avoid a doping effect by oxygen.²¹ A paramagnetic susceptibility was measured for C-1 between 7 and 300 K with a JEOL ME3X CW ESR spectrometer at X band (9.1 GHz). The temperature dependence of the susceptibility was determined from the comparison of the integrated ESR intensity calculated using JEOL ESPRIT-425 with an external reference (Mn^{2+} -MgO solid solution) which was simultaneously recorded and kept at room temperature. Spin-lattice relaxation time T_1 was measured with a JEOL PX1050 FT-ESR spectrometer at X band using an inversion recovery pulse sequence (180° - τ - 90°), while spin-spin relaxation time T_2 was determined with the FT-ESR spectrometer using a free-induction decay (FID) signal.

III. RESULTS

Temperature dependence of χT (χ is the total susceptibility) in C-1 is shown in Fig. 1. The gradual increase of χT depending on temperature is indicative of the deviation from the Curie law. Judging from the recent reports on the observation of temperature-independent (Pauli-like) susceptibilities,¹¹⁻¹³ we consider that the increase of χT originates from the Pauli-like component. In this point of

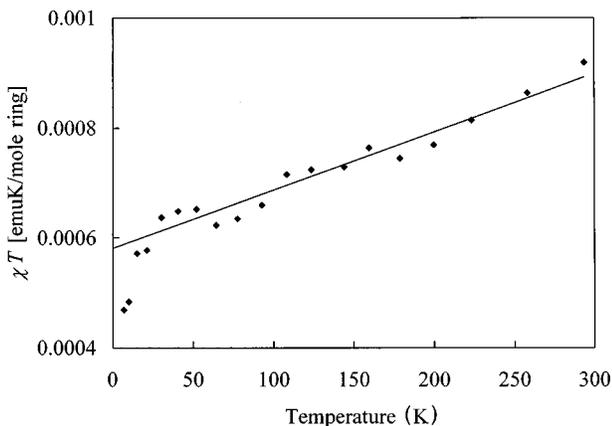


FIG. 1. χT plot in sample C-1. A solid line represents a linear fitting according to $\chi T = \chi_p T + C$. Thus, the slope and the intercept correspond to χ_p and C , respectively.

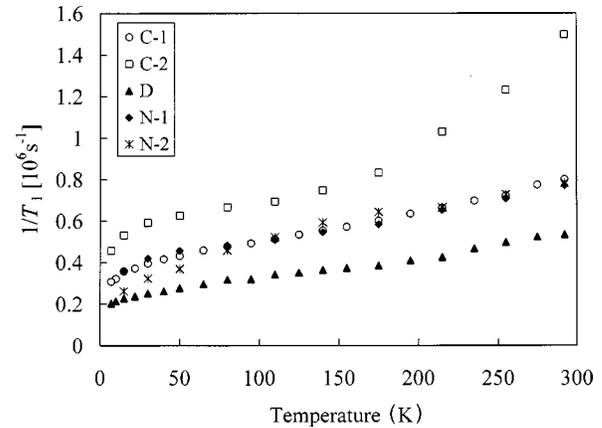


FIG. 2. Temperature dependence of spin-lattice relaxation rate T_1^{-1} for all the samples.

view, a linear fitting according to $\chi T = \chi_p T + C$ gives the Curie constant $C = 5.8 \times 10^{-4}$ emu K/mole-ring and the Pauli-like susceptibility $\chi_p = 1.1 \times 10^{-6}$ emu/mole-ring. The latter value, much smaller than the recent reports on heavily doped PPy (for example, 1.0×10^{-5} emu/mole-ring¹²), demonstrates that the decrease in doping level leads to a diminishment in the Pauli-like susceptibility.

CW ESR spectra of all the samples consisted of single lines with no hyperfine splitting and exhibited almost the same g values 2.0025, typical of π -conjugated compounds. All of the CW ESR spectra were extremely narrowed (for example, 1.8×10^{-2} mT at 298 K in C-1) and can be approximately fitted via Lorentzian curves without any anisotropies.

In the whole temperature range measured, the logarithm plots of one-pulse FID signals in all the samples sufficiently comprised straight lines, corresponding to Lorentzian curves in CW spectra. The refocusing of spin packets were not detected from a two-pulse sequence (90° - t - 180° - t) typical of conventionally generating spin echoes.^{22,23} In addition, the phase memory time (T_M) determined from the pulse sequence closely coincided with T_2^* determined from the FID in the whole temperature range measured, for all the samples. Therefore, under this situation, the relation is fulfilled that $T_2^* \approx T_M \approx T_2$. These findings demonstrate that the inhomogeneity in local fields around electron spins is averaged out due to the higher mobility of the spins compared to the spectral width in the Larmor frequency.

Spin-relaxation rates T_1^{-1} and T_2^{-1} of all the samples are shown in Figs. 2 and 3, respectively. These results reveal that the temperature dependences are typical of a motional narrowing effect, as expressed via the decreasing function of temperature in T_2^{-1} . Several differences are ascertained among the samples. First, both of the spin relaxation rates in C-2 exhibit somewhat larger values compared to the other samples. Further, the difference between samples C-1 and D explicitly demonstrates that the deuteration of the pyrrole rings effectively causes the decreases in both of the spin relaxation rates, similarly to the reports for t -PA.^{18,19} In contrast, remarkable differences between N-1 and N-2, including C-1, are hardly derived. This result indicates that the hyperfine coupling with nitrogen in NO_3^- scarcely contributes to the spin-relaxation rates, thus leading to the finding that the

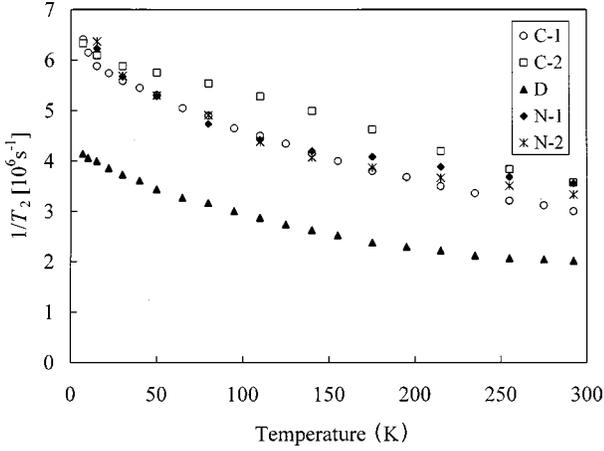


FIG. 3. Temperature dependence of spin-spin relaxation rate T_2^{-1} for all the samples.

electron spin density on each dopant anion is small in these lightly doped PPy.

IV. THEORY AND INTERPRETATION

A. Quantitative treatment of spin relaxation due to hyperfine interaction

The quantitative treatment of spin relaxation was proposed by Bloembergen, Purcell, and Pound²⁴ and completed by Kubo and Tomita.²⁵ It has been manifested that the theory is effective to interpret the spin-relaxation mechanism in NMR as well as in ESR. Expressions for the contribution of the electron-electron dipole interaction to electron-spin relaxation are similar to the case treated for the interaction between nuclei in NMR, but spin species precessing with an off-resonating frequency give a different influence from the above case on spin relaxation. According to the treatment by Abragam,²⁶ the general formulas for spin-relaxation rates caused by the dipole term in hyperfine interaction are

$$1/T_{1,hd} = \gamma_S^2 \gamma_I^2 \hbar^2 I(I+1) \{ 1/12 J^{(0)}(\omega_S - \omega_I) + 3/2 J^{(1)}(\omega_S) + 3/4 J^{(2)}(\omega_S + \omega_I) \} \quad (1)$$

$$1/T_{2,hd} = \gamma_S^2 \gamma_I^2 \hbar^2 I(I+1) \{ 1/6 J^{(0)}(0) + 1/24 J^{(0)}(\omega_S - \omega_I) + 3/4 J^{(1)}(\omega_S) + 3/2 J^{(1)}(\omega_I) + 3/8 J^{(2)}(\omega_S + \omega_I) \}, \quad (2)$$

where S and I symbolize an electron and a nucleus (or nuclear spin), respectively, for gyromagnetic ratios (γ) and Larmor frequencies (ω). Also the spectral density $J^{(j)}(\omega)$ are given by the Fourier transform of the autocorrelation function $G^{(j)}(\tau)$ as

$$J^{(j)}(\omega) = \int_{-\infty}^{\infty} G^{(j)}(\tau) \exp(-i\omega\tau) d\tau. \quad (3)$$

Then, assuming an isotropic motion, $G^{(j)}(\tau)$ are correlated with the random functions $F^{(j)}$ concerning the relative positions of two spins (r, θ, φ) as follows:

$$\delta_{jj'} G^{(j)}(\tau) = \overline{F^{(j)}(t) F^{(j')}(t+\tau)} = \overline{|F^{(j)}(0)|^2} g(\tau), \quad (4)$$

$$F^{(0)} = \frac{1 - 3 \cos^2 \theta}{r^3}, \quad F^{(1)} = \frac{\sin \theta \cos \theta e^{-i\varphi}}{r^3},$$

$$F^{(2)} = \frac{\sin^2 \theta e^{-2i\varphi}}{r^3}, \quad (5)$$

where upper lines are used to represent the ensemble average over all orientations. Thus, $J^{(j)}(\omega)$ are obtained by, using the Fourier transform $\phi(\omega)$ of $g(\tau)$,

$$J^{(j)}(\omega) = \overline{|F^{(j)}(0)|^2} \int_{-\infty}^{\infty} g^{(j)}(\tau) \exp(-i\omega\tau) d\tau$$

$$= \overline{|F^{(j)}(0)|^2} \phi(\omega). \quad (6)$$

For randomly oriented samples, the ensemble average are readily found as

$$\overline{|F^{(0)}(0)|^2} = \overline{(1 - 3 \cos^2 \theta)^2} \langle 1/r^3 \rangle^2 = 4/5 \langle 1/r^3 \rangle^2,$$

$$\overline{|F^{(1)}(0)|^2} = \overline{(\cos \theta \sin \theta e^{-i\varphi})^2} \langle 1/r^3 \rangle^2 = 2/15 \langle 1/r^3 \rangle^2,$$

$$\overline{|F^{(2)}(0)|^2} = \overline{(\sin^2 \theta e^{-2i\varphi})^2} \langle 1/r^3 \rangle^2 = 8/15 \langle 1/r^3 \rangle^2. \quad (7)$$

Here, the angular brackets indicate an average taken over the electric wave function. Therefore, defining that

$$\gamma_I^2 \hbar^2 \langle 1/r^3 \rangle^2 = B^2, \quad (8)$$

Eqs. (1) and (2) are reduced to

$$\frac{1}{T_{1,hd}} = \frac{2}{3} \gamma_S^2 I(I+1) B^2 \phi(\omega), \quad (9)$$

$$\frac{1}{T_{2,hd}} = \frac{1}{3} \gamma_S^2 I(I+1) B^2 \{ \phi(0) + \phi(\omega) \}, \quad (10)$$

under the approximation that $\omega_I/\omega_S \ll 1$. Hereafter ω is substituted for ω_S .

The contribution of the isotropic hyperfine interaction to electron-spin-relaxation rates is also given by Abragam:²⁶

$$\frac{1}{T_{1,hi}} = \frac{1}{3} \gamma_S^2 I(I+1) A^2 \phi(\omega), \quad (11)$$

$$\frac{1}{T_{2,hi}} = \frac{1}{6} \gamma_S^2 I(I+1) A^2 \{ \phi(0) + \phi(\omega) \}, \quad (12)$$

where A represents an isotropic hyperfine field by a nucleus.

In PPy, there exist several nuclear spins interacting with electron spins, and the strength may be different even among the same kind of nuclei. However, the effects of the same kind of nuclei on the electron-spin relaxation are commonly observed without distinguished. Also, considering that the spin relaxation is induced only through the fluctuation resulting from the electron-spin motion, an identical $\phi(\omega)$ is allowed over all the nuclei. Therefore, eventually, two spin-relaxation rates due to the hyperfine interactions are obtained as follows:

$$\frac{1}{T_{1,h}} = \gamma_S^2 \sum_{n,i} \rho_{n,i}^2 \hbar_n \phi(\omega), \quad (13)$$

$$\frac{1}{T_{2,h}} = \frac{1}{2} \gamma_S^2 \sum_{n,i} \rho_{n,i}^2 h_n \{ \phi(0) + \phi(\omega) \}, \quad (14)$$

where

$$h_n = \frac{1}{3} I_n(I_n + 1)(A_n^2 + 2B_n^2) \propto \gamma_n^2 I_n(I_n + 1), \quad (15)$$

and $\rho_{n,i}$ indicates the spin density on each nucleus.

B. Q1D diffusion model

In this section, the result of spin-relaxation rates are interpreted in terms of a one-dimensional (1D) diffusion model along a chain. The spectral density for the 1D diffusion has been proposed by many authors.^{7,9,27-29} Here we analyze our data according to the quasi-one-dimensional (Q1D) model in Ref. 9.

The solution for the 1D diffusion equation $\partial g / \partial t = D_{\parallel} \Delta g$ (D_{\parallel} is the diffusion constant along a chain) gives the probability density $g_{1D}(t)$ as

$$g_{1D}(t) = \frac{1}{\sqrt{4\pi D_{\parallel} t}} \exp\left\{-\frac{(|r_1 - r_2|/c)^2}{4D_{\parallel} t}\right\}, \quad (16)$$

where a diffusion rate D'_{\parallel} is defined by $D'_{\parallel} = D_{\parallel}/c^2$ (c is the lattice constant). A cutoff of the 1D motion is taken into consideration through assuming the escape probability from the 1D chain as $g_{\perp}(t) = \exp(-|t|/\tau_{\perp})$. Then, the probability density for the quasi-1D motion is obtained as

$$g_{Q1D}(t) = g_{1D}(t) \cdot g_{\perp}(t) = \frac{\exp(-|t|/\tau_{\perp})}{\sqrt{4\pi D'_{\parallel} t}} \exp\left\{-\frac{(|r_1 - r_2|/c)^2}{4D'_{\parallel} t}\right\}. \quad (17)$$

Therefore, after the Fourier transform of Eq. (17), $\phi_{Q1D}(\omega)$ is approximated by⁹

$$\phi_{Q1D}(\omega) \approx \frac{1}{\sqrt{2D'_{\parallel}/\tau_{\perp}}} \left(\frac{1 + \sqrt{1 + \omega^2 \tau_{\perp}^2}}{1 + \omega^2 \tau_{\perp}^2} \right)^{1/2}. \quad (18)$$

As the contribution to the electron-spin-relaxation rates, there are several elements to be taken into consideration; for the soliton in *t*-PA, the relaxation rates have been analyzed mainly on the basis of the dipole interaction between electron spins. Here, we treat the influence of a deuteration through the differences of the spin-relaxation rates at each temperature, under the assumption that the electron-spin dynamics is not affected by the deuteration. Thus we obtain from Eqs. (13) and (14)

$$\frac{1}{T_{1,H}} - \frac{1}{T_{1,D}} = \gamma_S^2 \sum_i \rho_{H,D,i}^2 (h_H - h_D) \phi(\omega), \quad (19)$$

$$\frac{1}{T_{2,H}} - \frac{1}{T_{2,D}} = \frac{1}{2} \gamma_S^2 \sum_i \rho_{H,D,i}^2 (h_H - h_D) \{ \phi(0) + \phi(\omega) \}, \quad (20)$$

where the spin density $\rho_{H,D,i}$ can be used in common for a proton and a deuterium. Therefore, substituting Eq. (18) for Eqs. (19) and (20), the cutoff frequency $1/\tau_{\perp}$ is given by

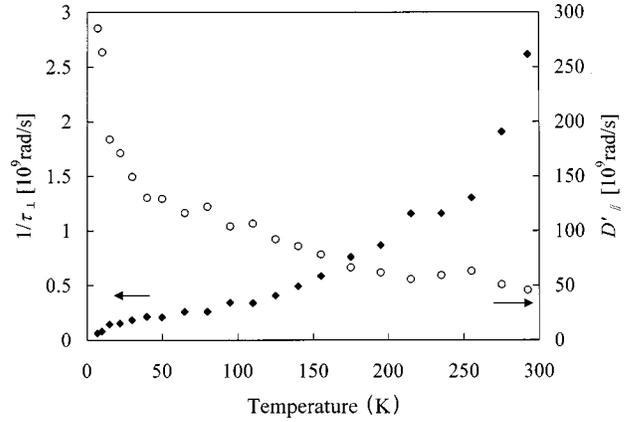


FIG. 4. Temperature dependences of the cutoff frequency $1/\tau_{\perp}$ estimated from Eq. (21) (filled diamond) and the diffusion rate along the chain D'_{\parallel} estimated from Eq. (22) (open circle).

$$1/\tau_{\perp} = \omega \left[\frac{4}{(\sqrt{8/(2\nu-1)^2 + 1} - 1)^2} - 1 \right]^{-1/2}, \quad (21)$$

where

$$\nu = \frac{1/T_{2,H} - 1/T_{2,D}}{1/T_{1,H} - 1/T_{1,D}}.$$

Then, temperature dependence of $1/\tau_{\perp}$ calculated from Eq. (21) is shown in Fig. 4. This result implies that $1/\tau_{\perp}$ gradually increases depending on temperature. Moreover, from the substitution of Eq. (18) for Eqs. (19) and (20), the diffusion rate along the chain is obtained as follows:

$$D'_{\parallel} = \frac{\gamma_S^4 \left(\sum_i \rho_{H,D,i}^2 \right)^2 (h_H - h_D)^2 \tau_{\perp} (1 + \sqrt{1 + \omega^2 \tau_{\perp}^2})}{2(1/T_{1,H} - 1/T_{1,D})^2 (1 + \omega^2 \tau_{\perp}^2)}. \quad (22)$$

In order to calculate the diffusion constant according to Eq. (22), $\sum_i \rho_{H,D,i}^2$ and $h_H - h_D$ have to be estimated. Yet, since those values are considered to be almost independent of temperature, assuming that $\sum_i \rho_{H,D,i}^2 = 0.3$ and $h_H - h_D = 2 \text{ mT}^2$, the rough estimate of the diffusion rate is obtained as shown in Fig. 4. This result implies that D'_{\parallel} in our sample decreases depending on temperature. This nonactivated type of 1D diffusion is opposite to the case in the neutral solitons,⁹ where a rapid increase depending on temperature was observed. As one interpretation, such a temperature dependence may result from an almost free rapid motion of spins within a chain domain.²⁰ The magnitude of D'_{\parallel} , however, is too small to be interpreted as such a rapid motion; actually, our D'_{\parallel} is almost two orders smaller than that of the neutral solitons.⁹ Furthermore, the ratio of D'_{\parallel} to $1/\tau_{\perp}$ is not so large to wholly regard the spin motion as quasi-one-dimensional, and then the predominant treatment of the 1D motion in $g(t)$ over the cutoff motion may be irrelevant. Therefore, from these opinions, we consider that the Q1D model is not necessarily suitable for elucidating the spin dynamics of our samples. This unsuitability is attributed to the lowly anisotropic motion of spins, thus leading to the finding that the one dimensionality of spin diffusion in these lightly doped PPy is small.

C. Random diffusion model

A highly one-dimensional diffusion of spins is generally considered to give a non-Lorentzian line shape. However, in diffusing between domains (chains) more rapidly than the Larmor frequency, the averaging effect over the domains yields a Lorentzian line shape. In this point of view, Lorentzian line shapes observed for our samples represent the presence of the higher cutoff diffusion between chains. Also from the previous section, the one dimensionality along the chains is presumed to be small. Thus, in this section, the data of spin-relaxation rates are interpreted in view of a random diffusion.

A random spin diffusion has been treated at first for NMR in liquid. Then, BPP proposed a exponential-type of correlation function,²⁴ and succeeded in evaluating the molecular motion. Thus, we simply assume that

$$g(t) = \exp(-|t|/\tau_c), \quad (23)$$

where τ_c is the correlation time. This assumption was similarly used for the cutoff frequency in the Q1D model. Here, it should be noted that the spin-correlation rate $1/\tau_c$ reflects a random, quasi-three-dimensional motion involving a 1D motion as well as a cutoff one. In this case, the Fourier transform of Eq. (23) is given as

$$\phi(\omega) = \frac{2\tau_c}{1 + \omega^2\tau_c^2}. \quad (24)$$

Then, substituting Eq. (24) for Eqs. (19) and (20), the spin-correlation rate is obtained using the differences of the spin-relaxation rates as

$$1/\tau_c = \frac{\omega}{\sqrt{2}}(\nu - 1)^{-1/2}, \quad (25)$$

where ν was already defined in Eq. (21). If all elements causing the spin-relaxation rates are expressed by forms similar to Eqs. (13) and (14), $1/\tau_c$ can be independently determined for the samples C-1 and D that, as we have already reported,¹⁷

$$1/\tau_c = \frac{\omega}{\sqrt{2}} \left(\frac{T_1}{T_2} - 1 \right)^{-1/2}. \quad (26)$$

Then two types of $1/\tau_c$ calculated from Eqs. (25) and (26) are shown in Fig. 5. These results demonstrate that two $1/\tau_c$ calculated from Eq. (26) for samples C-1 and D exhibit almost the same values and that those values are close to $1/\tau_c$ calculated from Eq. (25). Also, in both of the cases, the correlation rates increase with the rise of temperature, exhibiting a typical behavior in a activated type of spin motion.

From the substitution of Eq. (24) for Eqs. (19) and (20), the additional parameter can be derived as follows:

$$\sum_i \rho_{H,D,i}^2 (h_H - h_D) = \frac{\omega}{\sqrt{2}\gamma_S^2} (\theta - 1)^{-1/2} \{ (1/T_{2,H} - 1/T_{2,D}) - 1/2(1/T_{1,H} - 1/T_{1,D}) \}. \quad (27)$$

This parameter corresponds to the difference of the squared effective hyperfine fields between a proton and a deuterium.

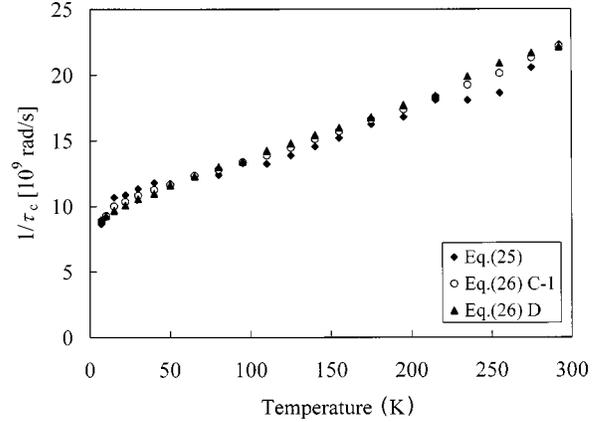


FIG. 5. Temperature dependence of the correlation rate $1/\tau_c$ estimated from Eqs. (25) and (26).

In addition, under the above-mentioned assumption made for Eq. (26), the next parameter can be determined independently for the samples C-1 and D,

$$\sum_{n,i} \rho_{n,i}^2 h_n = \frac{\omega}{\sqrt{2}\gamma_S^2} \frac{1/T_2 - 1/(2T_1)}{(T_1/T_2 - 1)^{1/2}}. \quad (28)$$

This parameter is the sum of the squared effective fields in the spin relaxation. Temperature dependences of both parameters determined from Eqs. (27) and (28) are shown in Fig. 6. Here, it is demonstrated that the difference of the parameters from Eq. (28) between samples C-1 and D closely coincides with the parameter from Eq. (27) in the whole temperature range and that those parameters are almost independent of temperature. The former finding clearly indicates the validity of the assumption that all the contributions to the spin relaxation are expressed by forms like Eqs. (13) and (14), as shown for $1/\tau_c$ as well, suggesting that the hyperfine interaction is the main contribution to the electron-spin-relaxation rates. Although the spin-density distribution may somewhat change depending on temperature, the total spin density over all protons or deuteriums is considered to be nearly constant in the whole temperature range. In this sense, the temperature-independent parameters derived from this analy-

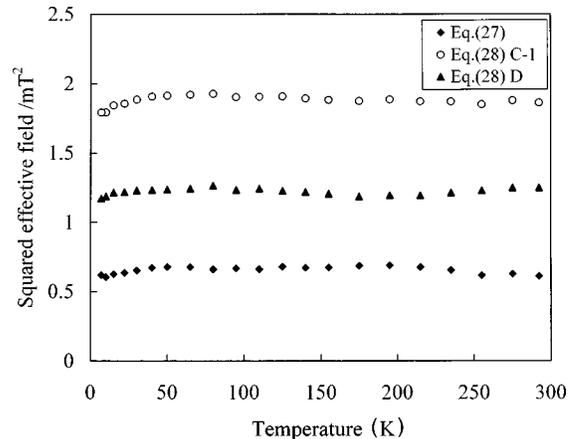


FIG. 6. Temperature dependences of the difference of the squared effective fields between a proton and a deuterium estimated from Eq. (27) and the sum of the squared effective fields estimated from Eq. (28) for the samples C-1 and D.

sis yield reasonable consequences as the effective hyperfine fields. In addition, those values give an estimate of $\sum_i \rho_{H,D,i}^2 \approx 0.3$ for $h_H - h_D = 2 \text{ mT}^2$, which is relatively appropriate as a physical picture.

Considering the result of $1/\tau_c$ that two correlation rates of samples C-1 and D are almost equivalent, our treatment in this section yields the reasonable explanation that the difference of spin-relaxation rates between samples C-1 and D originates only from that of the squared effective hyperfine fields. Therefore, we consider that the random diffusion model is suitable to interpret the spin-relaxation data for our samples. This indicates at the same time that the observed spins and polarons diffuse quasi-three dimensionally.

V. DISCUSSION

A. Origin of observed electron spins

The susceptibility of C-1 was well explained as the sum of a Curie term and a Pauli-like one. Generally, those terms are characteristic of localized and nonlocalized spins, respectively. On the other hand, our FID signals indicate that only one spin species is detected in the whole temperature range. The discrepancy should be discussed.

The absence of a spin echo in the two-pulse experiment indicates that wholly localized spins as observed in *t*-PA as trapped solitons are not involved in the ESR spectra. In contrast, the Elliott-type behavior typical of metallic conductors was demonstrated to be absent in T_2^{-1} . These observations suggest that the observed spins do not exist as definite species like Curie or Pauli types but belong to intermediate states between them. An inhomogeneous doping and a non-uniform chain length make it difficult to consider all possible sites of spins to be equivalent. Thus observed spins are anticipated to exist with a spread over possible levels. In this sense, we consider that the susceptibility expressed as the superposition of the two terms approximately reflects an averaged spin level. Single exponential FID curves as well as the motional narrowing behavior in the spin-relaxation rates are explicitly indicative of the existence of a rapid spin motion represented *via* the spin-correlation rate. The motion is considered to be a rapid diffusion over possible spin levels.³⁰ From these views, we conclude that observed spins exist over all possible spin levels and that the averaged behavior of those spins has been monitored in the analysis of the spin-relaxation rates.

B. Further discussion using the random diffusion model

In this section, all the spin-relaxation data are analyzed in terms of the random diffusion model using Eqs. (26) and (28). Figure 7 shows the spin-correlation rates for all the samples determined from Eq. (26), and the sums of the squared effective fields for all the samples estimated from Eq. (28) are shown in Fig. 8. The agreement among samples C-1, N-1, and N-2 is satisfactorily fulfilled in the two figures, indicating that the spin-relaxation mechanism is independent of the kind of dopant anions. On the other hand, sample C-2 exhibits somewhat different behaviors in the two parameters. The sum of the effective field in C-2 is larger than other samples. Concerning the hyperfine field, the increase depending on the doping level may be questionable. This be-

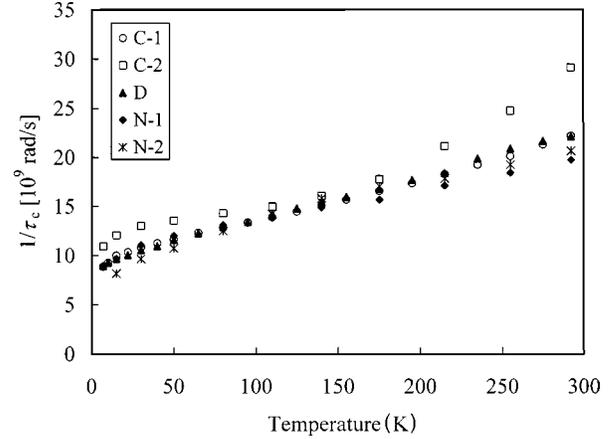


FIG. 7. Temperature dependence of the correlation rate $1/\tau_c$ estimated from Eq. (26) for all the samples.

havior is probably due to not considering the electron-electron dipole interaction. Actually, in considering such an interaction, the contribution of $\phi(2\omega)$ should be taken into account in Eqs. (13) and (14). Yet, it is worth noting that, under the condition that $\omega^2 \tau_c^2 \gg 1$,

$$\phi(2\omega) = \frac{\tau_c}{1 + 4\omega^2 \tau_c^2} \approx \frac{1}{4} \frac{\tau_c}{\omega^2 \tau_c^2} \approx \frac{1}{4} \phi(\omega).$$

Thus, in this case, the contribution of the electron-electron dipole interaction can be involved as a part of the sum of the effective fields. Such a condition is approximately fulfilled at low temperature in Fig. 7 ($\omega \approx 57 \times 10^9 \text{ rad/s}$). Therefore, the larger sum of the field in C-2 is considered to originate from the electron-electron dipole interaction, which is probably enhanced by the increase of spin concentration depending on the doping level. In other samples as well, the sums of effective fields may contain such contributions, which are probably not so large as to influence the estimate of several parameters so long as they are compared with the hyperfine field by a proton. Thus, the electron-electron dipole interaction is presumed to be relatively small in our samples, which is one of the reason for extremely narrowed ESR spectra. Also, Fig. 8 suggests that the sum of the effective field in C-2 is somewhat enhanced by increasing temperature above

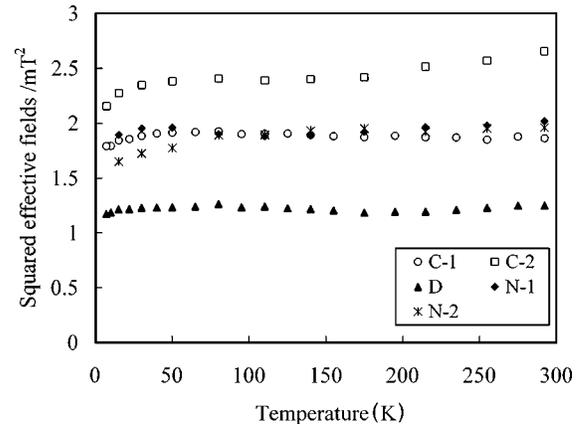


FIG. 8. Temperature dependences of the sum of the squared effective fields estimated from Eq. (28) for all the samples.

around 150 K. A similar behavior was observed in the heavily doped PPy,¹⁷ where the Elliott mechanism¹⁵ appears to almost govern the temperature dependence of T_2^{-1} . Hence, this enhancement of the sum implies that the Elliott type of behavior begins to develop at this doping level, and that our model may be insufficient for C-2 in this temperature range.

In Fig. 7, the spin-correlation rate of C-2 is suggested to be larger than those of other samples in the whole temperature range. The increase of the doping level is generally considered to enhance the Pauli susceptibility in conjugated polymers. In this sense, considering that the averaged behavior of all the spins existing in possible spin levels is monitored, this enhancement of $1/\tau_c$ is interpreted as attributed to the increment in the contribution of rapid spins resulting from the increment in the Pauli susceptibility.

C. Data evaluation of spin-correlation rates

As we have mentioned above, the spin-correlation rate $1/\tau_c$ reflects a quasi-three-dimensional spin motion. That is, this parameter enables the elucidation of polaron dynamics. Here, a physical interpretation of $1/\tau_c$ is discussed.

Our spin-relaxation data have been analyzed on the assumption that

$$\overline{F(t)F(t+\tau)} = \overline{F(0)}^2 \exp(-|\tau|/\tau_c), \quad (29)$$

where $F(t)$ represents a local field at a time t . Here, $F(t)$ can be assumed to be proportional to the probability $P(t)$ that after a time t , a spin exists at the initial site. Then, using the 1D random-walk model as a simple case, the next equation is obtained

$$\frac{dP(n,t)}{dt} = W \left[\frac{1}{2}P(n+1,t) + \frac{1}{2}P(n-1,t) - P(n,t) \right], \quad (30)$$

where W is a hopping probability per second. It should be noted that this equation is usually used under the condition that W is equivalent over all sites, at any time. Actually, however, a memory of a previous motion is not wholly removed, and hence, just after one hopping assisted by phonon, residual momentum will make the reverse hopping somewhat difficult. In that case, two terms, $P(n+1,t)$ and $P(n-1,t)$, are considered to fall after many hopping motions in a remarkable manner. Then, the solution of Eq. (30) comes close to the form of Eq. (29), and then $1/\tau_c$ corresponds to W . Therefore, in this case, $1/\tau_c$ approximately represents an actual hopping rate.

Given the hopping rate W , the mobility μ can be estimated by way of Einstein's relation,

$$\mu = \frac{eD}{k_B T} = \frac{eb^2W}{k_B T} \approx \frac{eb^2}{\tau_c k_B T}, \quad (31)$$

where b is the interchain distance. Taking b as 5 Å, the mobility of sample C-1 at room temperature is obtained as $2 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This is a typical value for the hopping mobility.³¹ Therefore, $1/\tau_c$ is presumed to be appropriate for an estimate of a hopping rate. In this sense, however, ap-

proximately linear temperature dependences of $1/\tau_c$ in Fig. 7 mean that b^2 dominates the temperature dependences of μ . Then, as one interpretation, the theory of variable range hopping³² suggests that μ decreases with the rise of temperature. This may be questionable and implies one possibility that the temperature dependence of $1/\tau_c$ may gradually include the effect of a spin exchange usually enhanced by a decrease in temperature. With respect to temperature dependence, further research may be necessary.

VI. CONCLUSIONS

We have examined the spin dynamics of polarons in lightly doped PPy on the basis of the temperature dependence of spin-relaxation rates measured with a pulsed ESR technique. The significant findings obtained here are summarized as follows.

Several experiments using pulse equipment have indicated that observed species are averaged out over several sites as if they were composed of one type, while the susceptibility data suggest the coexistence of Pauli and Curie types of spins. We conclude that the discrepancy is caused by the rapid diffusion of spins existing over possible spin levels. The spin-relaxation rates scarcely changed for a variety of dopants, indicating a minor electron-spin density on the dopants. On the other hand, we observed remarkable decreases resulting from the deuteration of PPy in T_1^{-1} as well as T_2^{-1} . Two models, the Q1D diffusion model and the random diffusion model, were proposed to elucidate the decreases in T_1^{-1} and T_2^{-1} . We point out that the Q1D model is not necessarily suitable for spins diffusing quasi-three dimensionally. In contrast, the random diffusion model can successfully interpret the decreases resulting from the deuteration in T_1^{-1} and T_2^{-1} as attributed to the difference in local fields (hyperfine field), independently of the temperature.

In the random diffusion model, the spin-correlation rate $1/\tau_c$ was used as a parameter to monitor the spin dynamics. This parameter is considered to give an estimate of the hopping rate for polarons in lightly doped PPy. Here, we point out that the quasi-three dimensionality of the hopping motion probably comes from the enhanced interchain interaction by the dopants. In this sense, our results suggest that dopant anions work as tunneling bridges between neighboring chains, as proposed by Zuppiroli *et al.*³³

The increase in the doping level was suggested to give a larger spin-correlation rate. This enhancement of $1/\tau_c$ is concluded to result from the increment in rapid spins. All the contribution of T_1^{-1} and T_2^{-1} were almost expressed as the forms like Eqs. (13) and (14), respectively. These findings mean that several spin-lattice-relaxation mechanisms *via* phonons²⁶ are ruled out for the interpretations. We point out that our treatment can give a significant explanation for the spin-relaxation behaviors mainly governed by a narrowing effect resulting from the quasi-three-dimensional motion.

ACKNOWLEDGMENTS

This work was supported in part by Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture (No. 10554031). One of the authors (K.K.) acknowledges the grant from the Japan Society for the Promotion of Science for Young Scientists.

- ¹H. Shirakawa, I. Ito, and S. Ikeda, *Makromol. Chem.* **179**, 1565 (1978).
- ²W. P. Su, J. R. Schrieffer, and A. J. Heeger, *Phys. Rev. Lett.* **42**, 1698 (1979).
- ³M. Nechtschein, F. Devreux, R. L. Greene, T. C. Clarke, and G. B. Street, *Phys. Rev. Lett.* **44**, 356 (1980).
- ⁴P. K. Kahol, G. C. Clark, and M. Mehring, in *Conjugated Conducting Polymers*, edited by H. Kiess (Springer-Verlag, Berlin, 1992).
- ⁵K. Mizoguchi and S. Kuroda, in *Handbook of Organic Conductive Molecules and Polymers*, edited by H. S. Nalwa (Wiley, Sussex, 1997), Vol. 3.
- ⁶K. Kume, K. Mizuno, K. Mizoguchi, K. Nomura, J. Tanaka, M. Tanaka, and H. Fujimoto, *Mol. Cryst. Liq. Cryst.* **83**, 49 (1982).
- ⁷M. Nechtschein, F. Devreux, F. Genoud, M. Guglielmi, and K. Holczer, *Phys. Rev. B* **27**, 61 (1983).
- ⁸W. G. Clark, K. Glover, G. Mozurkewich, C. T. Murayama, J. Sanny, S. Etemand, and M. Maxfield, *J. Phys. (Paris), Colloq.* **44**, C3-239 (1983).
- ⁹K. Mizoguchi, S. Masubuchi, K. Kume, K. Akagi, and H. Shirakawa, *Phys. Rev. B* **51**, 8864 (1995).
- ¹⁰O. Chauvet, S. Paschen, L. Forro, L. Zuppiroli, P. Bujard, K. Kai, and W. Wernet, *Synth. Met.* **63**, 115 (1994).
- ¹¹R. S. Kohlman, J. Joo, Y. Z. Wang, J. P. Pouget, H. Kaneko, T. Ishiguro, and A. J. Epstein, *Phys. Rev. Lett.* **74**, 773 (1995).
- ¹²K. Mizoguchi, N. Kachi, H. Sakamoto, K. Kume, K. Yoshioka, S. Masubuchi, and S. Kazama, *Synth. Met.* **84**, 695 (1997).
- ¹³E. J. Oh, K. S. Jang, J. S. Suh, H. Kim, K. H. Kim, C. H. Yo, and J. Joo, *Synth. Met.* **84**, 147 (1997).
- ¹⁴F. Devreux and H. Lecavelier, *Phys. Rev. Lett.* **59**, 2585 (1987).
- ¹⁵R. J. Elliott, *Phys. Rev.* **96**, 266 (1954).
- ¹⁶K. Mizoguchi, M. Honda, N. Kachi, F. Shimizu, H. Sakamoto, and K. Kume, *Solid State Commun.* **96**, 333 (1995).
- ¹⁷K. Kanemoto, J. Yamauchi, and A. Adachi, *Solid State Commun.* **107**, 203 (1998).
- ¹⁸N. S. Shiren, Y. Tomkiewicz, T. G. Kazyaka, A. R. Taranko, H. Thomann, L. Dalton, and T. C. Clarke, *Solid State Commun.* **44**, 1157 (1982).
- ¹⁹K. Mizoguchi, K. Kume, and H. Shirakawa, *Solid State Commun.* **50**, 213 (1984).
- ²⁰B. H. Robinson, J. M. Schurr, A. L. Kwiram, H. Thomann, H. Kim, A. Morrobel-Sosa, P. Bryson, and L. R. Dalton, *J. Phys. Chem.* **89**, 4994 (1985).
- ²¹G. B. Street, T. C. Clarke, M. Krounbi, K. K. Kanazawa, V. Lee, P. Pfluger, J. C. Scott, and G. Weiser, *Mol. Cryst. Liq. Cryst.* **83**, 253 (1982).
- ²²*Modern Pulsed and Continuous-wave Electron Spin Resonance*, edited by L. Kevan and M. K. Bowman (Wiley, New York, 1990).
- ²³A. Schweiger, *Angew. Chem. Int. Ed. Engl.* **30**, 265 (1991).
- ²⁴N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.* **73**, 679 (1948).
- ²⁵R. Kubo and K. Tomita, *J. Phys. Soc. Jpn.* **9**, 888 (1954).
- ²⁶A. Abragam, *Principles of Nuclear Magnetism* (Oxford University Press, Oxford, 1961).
- ²⁷G. Soda, D. Jerome, M. Weger, J. Alizon, J. Gallice, H. Rovert, J. M. Fabre, and L. Giral, *J. Phys. (Paris)* **38**, 931 (1977).
- ²⁸F. Devreux, *Phys. Rev. B* **25**, 6609 (1982).
- ²⁹P. K. Kahol, M. Mehring, and X. Wu, *J. Phys. (Paris)* **46**, 1683 (1985).
- ³⁰Here, a spin exchange between observed spins is not necessarily taken into consideration because the behavior of spin-relaxation rates could be well explained without considering such an effect.
- ³¹E. M. Conwell, in *Handbook of Organic Conductive Molecules and Polymers*, edited by H. S. Nalwa (Wiley, Sussex, 1997), Vol. 4.
- ³²N. F. Mott and E. A. David, *Electronic Process in Noncrystalline Materials* (Oxford University Press, Oxford, 1979).
- ³³L. Zuppiroli, M. N. Bussac, S. Paschen, O. Chauvet, and L. Forro, *Phys. Rev. B* **50**, 5196 (1994).