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ESR LINEWIDTH IN CONDUCTING POLYMERS WITH FIVE-MEMBERED RING

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The ESR linewidths in polythiophene, poly(3-methylthiophene) and polypyrrole doped with ClO_4^- and AsF_6^- were measured as a function of temperature to study the dynamics of charged carriers with spin. The temperature dependence of the ESR linewidth can be understood in terms of the Elliott mechanism, characteristic for metallic electrons. Such an interpretation leads us to conclude that the electron scattering is not governed by potential of dopants, but by that on polymer backbone. In addition, the temperature dependence of the resistance ratio r_{VSC} obtained by voltage-shorted-compaction method was found to coincide with that of the linewidth qualitatively. We show that a simple one-dimensional model for the resistivity that takes the electron scattering only by $2k_F$-phonons into consideration can qualitatively well explain both the data.

Keywords: A: polymers, D: electronic transport, D: spin-orbit effects, E: electron paramagnetic resonance

Polythiophene (PT), poly(3-methylthiophene) (PMeT) and polypyrrole (PPy) have non-degenerate electronic ground state (Fig. 1). Instead of solitons in trans-polyacetylene, polarons and bipolarons are the elementary excitations produced by doping to introduce charge carriers [1]. With increasing the dopant concentration, such excitations increase to form a lattice. At higher concentrations, the system indicates a metallic behavior, for example Pauli-like susceptibility and a linear temperature dependence in the thermoelectric power [1,2]. The d.c. conductivity σ, however, shows semiconducting temperature dependence, $d\sigma/dT>0$, even at the highest concentration. This discrepancy has been interpreted as the conduction through semiconducting regions like inter-fibril hopping, inter-chain hopping and inter-metallic tunneling [1]. One of the experimental methods to avoid such an effect due to the semiconducting regions is the spin dynamics that measures the motion of charge carriers with spin by means of ESR [3-8]. The second is the voltage-shorted-compaction (VSC) method [2,9]. The present study demonstrates the third one utilizing the ESR linewidth produced by the Elliott mechanism via spin-orbit mixing between bands.

In the present paper, we report the temperature dependence of the ESR linewidth for three different polymers with five-membered unit as shown in Fig. 1. A source of the observed ESR linewidth can be ascribed to the Elliott mechanism [10,11]. It is well known that the Elliott mechanism for the electron spin relaxation via a spin-orbit interaction is usually inhibited in one dimensional (1-D) electronic systems because of a symmetry restriction [10,11]. The reason why the Elliott mechanism is allowed in one of the typical 1-D electronic systems is that the constituent molecule is missing an inversion symmetry [12]. From an atomic number dependence of the line broadening due to the Elliott mechanism, it is strongly suggested that the dopant atoms practically give no contribution to the linewidth. An analysis of the Elliott mechanism in these polymers can give information on the electronic structure [8]. A simple model for the electrical resistivity in the 1-D electronic system where $2k_F$ phonon plays an important role, can qualitatively account for the observed temperature

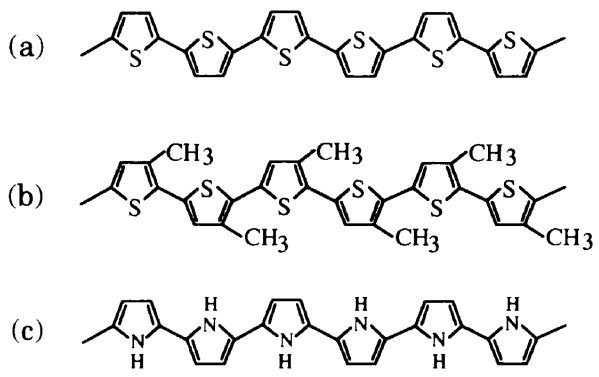

Fig. 1. Molecular structures for (a) polythiophene (PT), (b) poly(3-methylthiophene) (PMeT) and (c) polypyrrole (PPy).

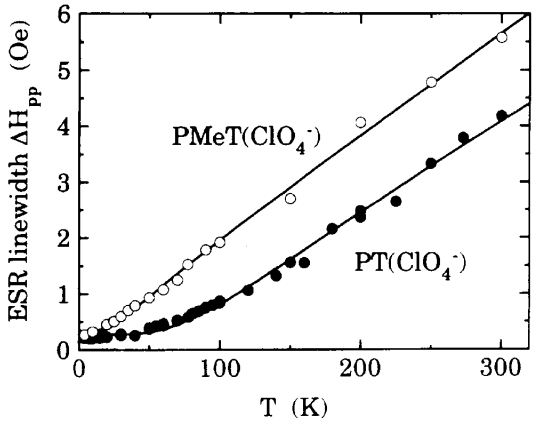

Fig. 2. The temperature dependence of the peak-to-peak ESR linewidth for PT(ClO_4^-) and PMeT(ClO_4^-). Note that the temperature variation in both samples is quite different. The solid curves, showing a prediction of eq. (2) with T_ω=240 K for PT(ClO_4^-) and 80 K for PMeT(ClO_4^-), qualitatively reproduce the ESR linewidth well.

dependence of the linewidth, together with the VSC resistance ratio r_{VSC} measured in the same batch as that for ESR. Here, r_{VSC} is defined as $R(T)_{VSC}/R(280\ K)_{VSC}$. It is noteworthy to stress that such a metallic behavior of r_{VSC} is reproducible up to 30~100 % of the samples studied, depending on polymer, dopant species and conditions in synthesis.

As-grown PT, PMeT and PPy films doped with ClO_4^- or AsF_6^- ion were prepared by the electrochemical synthesis as reported previously [2]. The dopant concentration was estimated as about 25 ~35 %/ring [2]. At a fixed frequency of 50 MHz, the temperature dependence of the ESR linewidth was measured between 4.2 and 300 K. Peak-to-peak ESR linewidth was determined by a least square fitting to the Lorentzian lineshape. VSC resistance ratio was measured in a conventional four terminal configuration on the films with an extremely thin layer of silver or gold paste [2,9].

Figures 2 shows the temperature dependence of the ESR linewidth for both PT(ClO_4^-) and PMeT(ClO_4^-) and Fig. 3 shows that in PPy(ClO_4^-). Since the observed lineshape is Lorentzian for all the measurements, it is concluded that the condition of extreme narrowing is satisfied in the present systems [13]. Furthermore, the positive temperature dependence of the ESR linewidth $d(\Delta H)/dT>0$ consistent with the reported data [14-16], cannot be explained in terms of the usual motional narrowing caused by the thermal motion of the electron spins. The above observation is natural for the ESR of conduction electrons in metals. In such a case the ESR linewidth is dominated by the life time broadening of Zeeman levels due to spin-lattice relaxation. For example, ESR in the alkali metals gives the Lorentzian lineshape and its linewidth is proportional to the square of ESR g-shift [17]. This behavior has been understood in terms of the relaxation mechanism via spin-orbit mixing of bands, which is known as the Elliott mechanism [10,11]. The Elliott mechanism provides the ESR linewidth, or equivalently the spin-spin relaxation rate, as written by the relation,

$$\Delta H \propto T_2^{-1} = a(\frac{\lambda}{\Delta E})^2 \tau^{-1} = a(\Delta g)^2 \tau^{-1} \propto \rho. \qquad (1)$$

Here, ΔH is the ESR linewidth, T_2^{-1} the spin-spin relaxation rate, λ the spin-orbit coupling constant, ΔE the energy difference between bands, τ^{-1} the relaxation rate of the electron momentum, a the numerical constant of the order of unity, Δg the ESR g-shift and ρ the electrical resistivity. A brief picture of this mechanism is that the spin-orbit mixing of two bands makes the matrix element between up and down spin states finite when the electron spin is scattered by phonon, impurity or disorder. Then, eq. (1) suggests that the ESR linewidth is expected to show the corresponding behavior to the electrical resistivity ρ qualitatively, when the ESR linewidth is dominated by the Elliott mechanism [11]. It is shown in Figs. 4 and 5 that the ESR linewidth substantially shows the corresponding behavior to the VSC resistance ratio in the wide temperature range from 20 to 300 K for PT(ClO_4^-) and PT(AsF_6^-).

Another evidence for the Elliott mechanism in the ESR linewidth is a significant difference in the linewidth between PT (~4 Oe at 300 K), PMeT (~6 Oe) and PPy (~0.2 Oe) systems. It is well-known

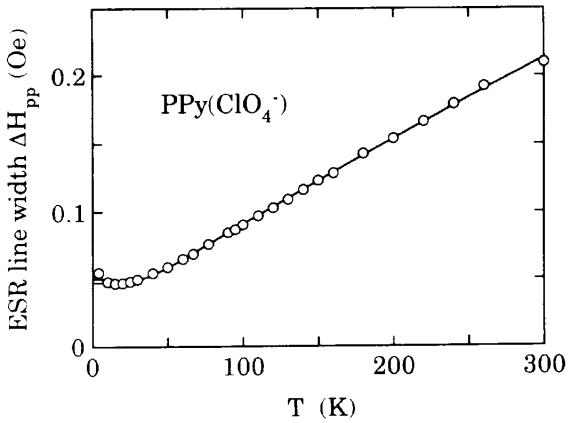

Fig. 3. The temperature dependence of the peak-to-peak ESR linewidth for PPy(ClO_4^-). Positive large intercept and smaller linewidth compared with that in Fig. 2 are characteristic. The solid curve shows eq. (2) with T_ω=130 K. The steep rise at the lowest temperatures may be due to the Curie contribution.

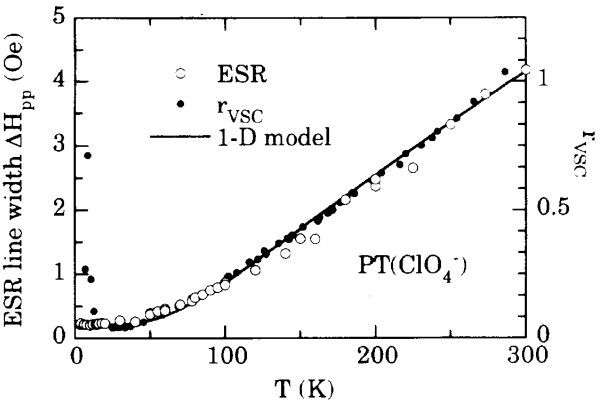

Fig. 4. The temperature dependence of the peak-to-peak linewidth together with r_{VSC}. The solid curve shows eq. (2). Both data can be qualitatively well reproduced by eq. (2). Origin of the steep rise below 30 K in r_{VSC} is suggested to be an indication of some phase transition [2].

that the spin-orbit coupling constant λ strongly depends on the atomic number z. Then, the heaviest atom of sulfur in thiophene and methylthiophene rings and nitrogen in pyrrole ring would play an important role for the linewidth. The ratio of ΔH(PMeT)/ΔH(PPy) $\approx 5.1^2$ can be compared with λ(PMeT)/λ(PPy) = 382 cm^{-1}/72 cm^{-1} $\approx$ 5.3 at 300 K. This coincidence between ΔH and λ suggests a dominance of the Elliott mechanism, if $\tau^{-1}/\Delta E^2$ is assumed to have the same magnitude in these systems. This supposition seems to be appropriate, since both polymers have isostructure and the same orders of conductivity around 300 K. In addition, it can be concluded that the massive atoms, chlorine and arsenic, in the dopant molecule have a negligible contribution to the ESR linewidth, because the heaviest chlorine atom in PPy(ClO_4^-) seems irrelevant to the linewidth and furthermore, there is no marked dependence on dopant species; ClO_4^- and AsF_6^- in the linewidth. This means that most of the charged carriers are not on the dopant molecule, but on the polymer chain backbone, inconsistent with the recent report that the dopant ion is important to provide a bridge for polaron to delocalize over two chains [18]. If this report is the case, the ESR linewidth would be expected to depend noticeably on λ for the constituent atoms of the dopant.

The same conclusion for the ESR linewidth to be dominated by the Elliott mechanism, is reported for TTF-TCNQ [12,19] and KCP [20], but with considerably different values of less than 0.01 for the parameter a in eq. (1). Such a small a has been rationalized by the symmetry restriction in 1-D systems for the Elliott mechanism. How about in the present systems ? The symmetry restriction can be applicable in the case where the incident electron with wave vector $\boldsymbol{k}$ is scattered to $-\boldsymbol{k}$, keeping an inversion symmetry. Then, the pure 1-D electronic systems where only $\Delta k = 2k_F$ scattering is effective, always satisfy the above condition and are not dominated by the Elliott mechanism. In the actual case, however, the Elliott mechanism is not restricted completely, but survives, since the dimensionality of the electronic system should be *quasi* 1-D. In the present case, the parameter a is found to be around unity [8], which definitely violates the symmetry restriction. This contradiction can be avoided for the systems with a five-membered ring: there is no inversion symmetry as shown in Fig. 1, resulting in no inversion symmetry in the Fermi surface. Furthermore, expected disorder in the arrangement of polymer crystal and dopant makes the Fermi-surface obscure to some extent. Therefore, the symmetry restriction can not be applied to the present case and the ESR linewidth shown in Figs. 2-5 is reasonably interpreted as a life time broadening by the Elliott mechanism. If one has g-shift data, $\Delta g = g_\perp - g_{//}$ for the axial symmetry case, the momentum relaxation rate τ^{-1} can be derived and gives information on the conductivity through the relation $\sigma_{D//} = ne^2\tau/m^*$, where n is the carrier concentration and m^* the effective mass of the carrier [8]. Although it is difficult to obtain Δg without single crystal, it

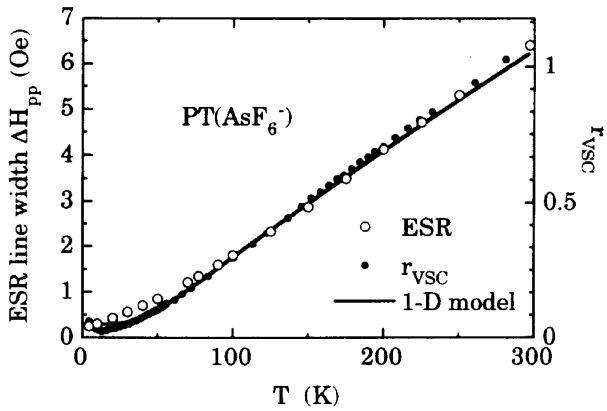

Fig. 5. The same plot as in Fig. 4 for polythiophene doped with AsF_6^- ion. The solid curve shows eq. (2) with T_ω=150 K which qualitatively well reproduces both the data.

becomes possible by studying the linewidth as a function of frequency. Such a study is in progress and will be reported soon.

The present systems exhibit a variety of the temperature dependences of the linewidth and the VSC resistivity ratio. It is linear in PMeT(ClO_4^-), but obeys second power law in PT(ClO_4^-). It is sublinear in PPy(ClO_4^-). To understand these differences we made a simulation of the qualitative temperature dependence using a simple model for the resistivity in 1-D electronic system. Provided that the electronic state of the present systems is highly one-dimensional [3,8] where $2k_F$- and/or nearly $2k_F$-phonons have major importance for the charge carrier scattering, the expression for the resistivity can be given by [3,21,22]

$$\rho=\rho_0+\frac{\pi^2\hbar\Sigma\alpha^2D(E_F)}{e^2M\omega_0v_F}\frac{1}{\cosh(T_\omega/2T)\sinh(T_\omega/2T)}, \quad (2)$$

where ρ_0 is the residual resistivity, Σ the cross-sectional area of the chain, α the electron-phonon coupling constant, $D(E_F)$ the density of states at the Fermi energy, $k_BT_\omega=\hbar\omega_0$, $\hbar\omega_0$ the energy of the $2k_F$-phonon and the other symbols have their usual meanings. Temperature dependence of eq. (2) is characterized by the parameter T_ω which is a measure of the $2k_F$ phonon frequency in unit of temperature. Above T_ω, eq. (2) increases linearly with temperature and below T_ω it decreases exponentially. T_ω obtained from Figs. 2-5 are listed in Table I. T_ω~1400 K has been estimated for metallic polyacetylene idealized to have no bond alternation with the unit cell length 1.23 Å (one electron per carbon) [22]. The significant disagreement

Table I T_ω's for the several conducting polymers with the five-membered ring, doped by ClO_4^- or AsF_6^-. T_ω is a measure of the frequency for the phonon with $q=2k_F$ in unit of temperature.

	PT(ClO_4^-)	PMeT(ClO_4^-)	PPy(ClO_4^-)	PT(AsF_6^-)
T_ω (K)	240	80	130	150

with the present result is due to a difference of the electronic states: $2k_F$ in the half-filled bands is equal to π/c with the unit cell size c and the dopant concentration determines the unit cell size c by its potential. Assuming a constant velocity for phonon, the lattice parameter along the polymer chain of ~4 Å and one hole carrier per 3 to 4 rings (25~30 % per ring) for the present systems give T_ω for the lowest phonon-branch as 1400×1.23/4/(4~3) ≈108~144 K that is consistent with the present one shown in Table I. If one assumes sinusoidal dispersion for the phonon, one gets larger T_ω than the above values by $\pi/2$. Such estimation can be practically applicable to the polyacetylene case. The dopant concentration is usually of the order of 10 % per carbon atom, which gives T_ω~140 K ($\times\pi/2$ =220 K for the sinusoidal phonon dispersion). Actually, T_ω~160 K has been found in the Br-doped polyacetylene studied by the spin dynamics with NMR [3,21]. The scatter in T_ω shown in Table I would be concerned with a difference of the electronic states in the host polymers and possibly with different dopant concentrations. Finally, note that the microscopic conductivity for PT(ClO_4^-) estimated by the spin dynamics with ESR was of the order of 1×10^3 S/cm at 300 K [8].

The following points should be noted in interpreting the linewidth in terms of the Elliott mechanism and the VSC resistance ratio. First, the ESR linewidth should be taken carefully at low temperatures below 50 K where the Curie susceptibility exceeds the Pauli susceptibility. Secondly, below 30 K in Fig. 3 an origin of the steep increase in r_{VSC} is not clarified yet: one possibility is proposed to be some phase transition [2], and the other is an appearance of semiconducting resistance due to the semiconducting regions. Thirdly, although eq. (2) can reproduce the present data qualitatively, it does not necessarily mean that eq. (2) is a unique functional form to do so.

In conclusion, the ESR linewidth has been shown to be dominated by the Elliott relaxation mechanism via spin-orbit coupling. This is a characteristic feature in the five-membered-ring polymers that has no inversion symmetry in the con-

stituent molecular unit. Therefore, the temperature dependence of the ESR linewidth represents that of the electrical resistivity. This point was successfully confirmed by comparing the ESR linewidth with the temperature dependence of the VSC resistance ratio. Furthermore, the obtained temperature dependence was qualitatively analyzed with a simple 1-D model for the electrical conductivity and the characteristic parameter of T_ω was obtained. The order of such T_ω's was found to be physically reasonable for the conducting polymers. Finally, the dopant atoms contribute very little to the Elliott broadening.

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References

1. For recent development on the conducting polymers, see, for example, Proc. Int. Conf. Sci. and tech. of Synth. Metals (ICSM'94), Seoul, 1994, Synth. Met. **69-71** (1995).
2. (1) S. Masubuchi, S. Kazama, K. Mizoguchi, H. Honda, K. Kume, R. Matsushita and T. Matsuyama, Synth. Met. **57**, 4962 (1993). (2) S. Masubuchi and S. Kazama, Synth. Met. in press.
3. K. Mizoguchi, Jpn. J. Appl. Phys. **34**, 1 (1995) and Makromol. Chem., Macromol. Symp. **37**, 53 (1990).
4. K. Mizoguchi, S. Masubuchi, K. Kume, M. Suezaki, K. Akagi and H. Shirakawa, Phys. Rev. **B51**, 8864 (1995).
5. K. Mizoguchi, M. Nechtschein, J.P. Travers and C. Menardo, Phys. Rev. Lett. **63**, 66 (1989).
6. K. Mizoguchi, M. Nechtschein and J.P. Travers, Synth. Met. **41**, 113 (1991).
7. K. Mizoguchi and K. Kume, Solid St. Commun. **89**, 971 (1994).
8. K. Mizoguchi, M. Honda, S. Masubuchi, S. Kazama and K. Kume, Jpn. J. Appl. Phys. **33**, L1239 (1994).
9. S. Masubuchi, K. Mizoguchi, K. Mizuno and K. Kume, Synth. Met. **22**, 41 (1987).
10. R.J. Elliott, Phys. Rev. **96**, 266 (1954).
11. Y. Yafet, *Solid State Physics* V14, Ed. H. Ehrenreich, F. Seitz, D. Turnbull, Academic, N.Y., (1965).
12. F. J. Adrian, Phys. Rev. **B5**, 2682 (1982).
13. A. Abragam, *Principles of Nuclear Magnetism*, chapter 8 (Oxford University, Oxford, 1961).
14. G. Tourillon, D. Gourier, P. Garnier and D. Vivien, J. Phys. Chem. **88**, 1050 (1984).
15. M. Scharli, H. Kiess, G. Harbeke, W. Berlinger, K. W. Blazey, K. A. Mullar, Synth. Met. **22**, 317 (1988).
16. N.S. Sariciftci, A. Grupp and M. Mehring, Chem. Phys. Lett. **192**, 375 (1992).
17. F. Beuneu and P. Monod, Phys. Rev. **B6**, 2422 (1978).
18. L. Zuppiroli, M.N. Bussac, S. Paschen, O. Chauvet and L. Forro, Phys. Rev. **B50**, 5196 (1994).
19. M. Weger, J. Phys. (Paris) **39**, C6-1456 (1978).
20. T. Takahashi, H. Doi and H. Nagasawa, J. Phys. Soc. Jpn. **48**, 423 (1980).
21. F. Shimizu, Doctor Thesis, Tokyo Metropolitan University in 1994, and F. Shimizu et al., to be published.
22. S. Kivelson and A.J. Heeger, Synth. Met. **22**, 371 (1988).