# ESR Study of Advanced Materials with New Parameters: Frequency and Pressure

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(August 22, 2000)

It is well known that Electron Spin Resonance (ESR) is a useful technique to investigate the magnetic properties of electrons in condensed matter. The frequency, as an additional parameter to the temperature, gives us the possibility to study the anisotropic dynamics of charge carriers with spin, even in polycrystalline materials. Furthermore, the pressure provides us a way to discuss how interactions between the electrons and their environments are responsible for the novel physical properties in these advanced materials, such as ferromagnetisms, charge-density waves, superconductivity, and so on. Results obtained by using ESR with these parameters are overviewed. Studies as a function of the frequency are demonstrated, especially for the conductive polymers, polyacetylene, polyaniline, and polypyrrole with various dopants for which single crystals are not available yet. Alkali-electro-sodalite (AES), a kind of zeolite with a regular electron lattice known as an *s*-electron Mott insulator, and fullerene compounds with ferromagnetism and antiferromagnetism are discussed as examples of the pressure study.

# I. INTRODUCTION

The electron Spin Resonance (ESR) technique enables us to obtain useful information on the electronic states in advanced materials such as conductive polymers [1]. Usually, commercial ESR spectrometers are operated at several fixed frequencies such as the X-band ( $\approx 9$  GHz) and exceptionally at the K- and the Q-bands ( $\approx 24$  and  $\approx$ 35 GHz). However, with the use of home-built spectrometers operated at arbitrary frequencies extending from MHz to tenths of GHz, a new category of information, spin dynamics, can be investigated. For the first time, such a study has been reported on the spin dynamics of neutral solitons in trans-polyacetylene [2,3]. After that, spin dynamics were applied to various conductive polymers to reveal the dynamics of spin-carrying charges, especially in crystalline regions, and demonstrated a remarkable difference in the transport property from that observed by using a conventional transport measurement with a four-terminal configuration [1,4-6].

Recently, we developed an ESR measurement technique under high pressure with a clamp-type cell [7]. High pressure enables us to tune the strength of the interactions between the electrons and is useful way to identify the major interaction dominating individual physical properties, such as ferromagnetism, antiferromagnetism, charge density wave (CDW), etc. For this purpose, it is important to do the investigation under both hydrostatic and uniaxial pressures. The latter enables us to enhance the interaction selectively along the concerned direction. In this report, some investigations of ESR as functions of not only the temperature but also the frequency and/or the pressure will be presented.

# II. EXPERIMENTAL

ESR is measured by home-built spectrometers in all frequency ranges. A loop-gap resonator and a cylindrical cavity is used for the tenths of GHz range instead of the coil used below the GHz range. The frequency of 130 Hz was utilized to modulate the static magnetic field. Such a low frequency is effective to avoid the skin depth effect even in the thick wall of a metallic pressure cell. ESR  $T_1^{-1}$  was measured with a saturation method. Hydrostatic pressures of up to  $\approx 20$  kbar were applied with a clamp-type cell made of CuBe alloy filled with Daphne 7373 oil as a pressure medium. Pistons are made of Zirconia, since a CuBe piston would be crushed by a pressure of 20 kbar. The pressure drop due to thermal contraction of the oil was accounted for by using the experimental data of Murata. [8]

# **III. RESULTS AND DISCUSSION**

## A. Frequency: Spin Dynamics Study

## 1. Principles

The ESR relaxation rates,  $T_1^{-1}$  and  $T_2^{-1}$  (a part of the line width), reflect the spectral intensities of the local fields fluctuating at the ESR Larmor frequency [9]. Then, if one measures the relaxation rates as a function of the frequency, the frequency spectrum of the fluctuating local fields can be determined. Such a spectrum contains information on the dynamics of the spin carriers. Imagine two linear chains on which the spin carriers diffuse rapidly with a diffusion rate D (sec<sup>-1</sup>) that is equal to a diffusion constant,  $\mathcal{D}$  (cm<sup>2</sup>/sec), divided by a square of the lattice constant,  $a^2$  (cm<sup>2</sup>). Each spin produces a time-dependent dipolar field modulated by the one-dimensional (1D) diffusive motion of the other. A resulting frequency spectrum produced by the 1D motion is obtained by solving a diffusion equation [9] or an anisotropic random walk equation [10], giving rise to a  $1/\sqrt{D_{\parallel}\omega}$  dependence. In the case of a 2D diffusive motion, one gets a log ( $\omega/D$ ) relation, and in the 3D case, the frequency spectrum is independent of  $\omega$  [10].

For the more realistic case of quasi-1D diffusive motion, the autocorrelation function  $\phi$  of the fluctuating local fields is expressed as [10]

$$\phi(\omega) = \frac{1}{\sqrt{4D_{\parallel}/\tau_{\perp}}} \sqrt{\frac{1 + \sqrt{1 + (\omega\tau_{\perp}/2)^2}}{1 + (\omega\tau_{\perp}/2)^2}},$$
 (1)

where  $\tau_{\perp}^{-1}$  is the cutoff frequency of the 1D correlation. With the use of Eq. (1), the relaxation rates for the electronic dipolar interaction are written as follows [9]:

$$T_1^{-1}(\omega) = \gamma_e^4 \hbar^2 S(S+1) c \Sigma_\ell [0.2\phi(\omega) + 0.8\phi(2\omega)], \quad (2a)$$

$$T_2^{-1}(\omega) = \gamma_e^4 \hbar^2 S(S+1) c \Sigma_\ell \times [0.3\phi(0) + 0.5\phi(\omega) + 0.2\phi(2\omega)], \qquad (2b)$$

where c is the spin concentration,  $\Sigma_{\ell}$  is the lattice sum, and the others have usual meanings. In actual cases, contributions other than only those in Eqs. (2) should be taken into account.

#### 2. Neutral Soliton in Trans-polyacetylene

The first example is the neutral soliton dynamics in pristine trans-polyacetylene (t-PA). As is well known, t-PA contains neutral defects of  $\approx 400$  ppm per carbon, customarily called neutral solitons, which are produced by a mismatching between two possible phases of bond alternation, as shown in Fig. 1. Here, it should be noted that both phases have the same ground state energy; a degenerate ground state is a requirement for stabilization of solitons. The neutral solitons are predicted theoretically to move freely along the chain [11]. Experimental evidence for the free motion has been obtained from ESR line width and NMR relaxation rate analyses [12,13]. Nevertheless, some questions have been raised about such interpretations [14]. Finally, analysis of ESR as a function of frequency has given firm evidence for the fast diffusive motion of neutral solitons, as described in Fig. 2 [2,3].



FIG. 1. The neutral soliton in t-(CH)<sub>x</sub>. The dot represents an unpaired electron, carrying spin 1/2, without charge.



FIG. 2. Frequency dependences of the spin-lattice relaxation rate in t-(CH)<sub>x</sub> and t-(CD)<sub>x</sub> [6]. The  $1/\sqrt{\omega}$  dependence in the high-frequency range is evidence for the 1D diffusive motion of neutral solitons. The inset demonstrates identification of relaxation mechanisms; the electronic dipolar interaction linearly depends on the soliton concentration c and the hyperfine interaction is independent of c and negligible for t-(CD)<sub>x</sub>.



FIG. 3. The temperature dependence of the diffusion rate along the chain,  $D_{\parallel}$  [6].

The solid curve for t-(CH)<sub>x</sub> in Fig. 2 represents a sum of Eq. (2a) and a corresponding relation for the hyperfine interaction [2]. On the other hand, the solid curve for t-(CD)<sub>x</sub> represents only the electronic dipolar contribution expressed by Eq. (2a), since the nuclear magnetic moments for the carbon and the deuteron are small enough to neglect their contributions to the ESR  $T_1^{-1}$ . These curves show a saturation below 10 MHz because of a cutoff in the correlation of the 1D diffusive motion caused by the hopping of spin carriers between chains or by other 3D interactions [15]. From these solid curves obtained with Eq. (2a) the diffusion rate  $D_{\parallel}$  at 300 K was deduced to be  $\approx 5 \times 10^{13}$  (rad/s) [3]. A similar study was done for ESR  $T_2^{-1}$  deduced from

A similar study was done for ESR  $T_2^{-1}$  deduced from ESR line width measurement down to 4.2 K [2]. The temperature dependence of  $D_{\parallel}$  is approximately proportional to  $T^2$ , as demonstrated in Fig. 3 [2]. These values were compared successfully with the theoretical predic3. Spin Dynamics in Polyaniline Protonated with HCl



FIG. 4. Structures of polyanilines: (a) emeraldine base (EB) and (b) HCl-protonated emeraldine salt (ES).



FIG. 5. The frequency dependence of the ESR line width in ES for various temperatures [5]: (a)  $T \ge 150$  K and (b)  $T \le 150$  K. The solid curves represent Eq. (2b).

The second example of a spin-dynamics study is charge transport in conductive polyaniline (PANI) [4,5]. The structures of PANI, insulating emeraldine base (EB) and conductive emeraldine salt (ES) protonated by HCl, are shown in Fig. 4. Since the ground-state energy of PANI does not degenerate for exchange of bond alternation, a polaron is a stable excitation, instead of a soliton in *t*-PA. A unique feature of the protonation is the creation of a polaron charge carrier, keeping the total number of electrons on the polymer chain constant upon protonation; a proton joins to a nitrogen whose positive charge is neutralized by a neighboring chlorine anion. Associated with the formation of polarons by full protonation, remarkable enhancements were reported in the conductivity, more than  $10^{10}$  times, up to 5 (S/cm) and in the number of electron spins, more than two orders of magnitude [18]. However, it is curious that the temperature dependence of the conductivity in ES shows a 1D variable-range-hopping (VRH) nature [18]. The probable reason is the sizable contribution of an interfacial, semiconducting part in the sample. Then, it would be interesting to apply the spin-dynamics method to ES to reveal the charge transport within the crystalline part of the sample.

Figure 5 shows the temperature variation of the ESR line width versus frequency in ES [1,5]. Note that, with increasing temperature, the cutoff frequency monotonously increases over the whole temperature range, but that the slope in the high-frequency range, which is proportional to  $1/\sqrt{D}$ , decreases below 150 K, goes through a minimum, and increases again above 150 K. The fitting parameters for these solid curves yield the temperature dependence of the diffusion rate along chain,  $D_{\parallel}$ , and of the cutoff frequency  $\tau_{\perp}^{-1}$ , as shown in Fig. 6.

An interesting feature is a metal-to-insulator transition of  $D_{\parallel}$  at 150 K for the fully protonated ES, which is a striking contrast to that of the conventional dc conductivity data described by open diamonds and open triangles in Fig. 6. For the sample with intermediate protonation, y=0.27, the transition temperature looks to be around 250 K. While the cutoff frequency,  $\tau_{\perp}^{-1}$ , shows good agreement with the dc conductivities above 100 K and 250 K for y=0.62 and 0.27, respectively. Then, it can be concluded in the present case that the cutoff frequency corresponds to the interchain hopping rate of the charge carriers with spin. Below such temperatures,  $\tau_{\perp}^{-1}$  loses its variation with temperatures because some 3D interaction interrupts the 1D correlation of the motion. Therefore, these charge-transport observations suggest that the dc conductivity is dominated by the interchain hopping of charge carriers.

A relatively large anisotropy of the charge transport, more than  $10^5$  at 150 K, is a characteristic feature in PANI. In the case of PANI doped with camphorsulfonic acid (CSA), the anisotropic feature is remarkably enhanced because of the large molecular size of the dopant [19]. The five-membered ring polymers, such as polypyrrole and polythiophene doped with various acceptors, exhibit a strong interchain coupling because of a face-toface stacking of the flat polymer chains [20]. As a result, the 1D charge transport is known to be much weaker than for PANI, giving rise to Elliott ESR line broadening through the spin-orbit interaction at the nitrogen and the sulfur atoms in these five-membered ring polymers [21]. Actually, the temperature dependences of the ESR line widths in polypyrrole and polythiophene could be interpreted by using the phonon-scattering mechanism for one-dimensional metals [1,6,22,23]. Interestingly, the temperature dependence of the resistance, obtained with a special technique to measure the resistance through only the crystalline region with extremely short spacing of the voltage terminals in a four-terminal configuration, was found to follow that of the Elliott ESR line width very well [1,22,23].



FIG. 6. The temperature dependences of the diffusion rate along chain  $D_{\parallel}$  and of the cutoff frequency  $\tau_{\perp}^{-1}$ , along with the dc conductivity [1].

# **B.** Pressure: Tuning of Intermolecular Interactions

#### 1. General View

Pressure changes the distances between atoms and molecules, thereby tuning the electron-electron and the electron-lattice interactions. In the cases of polymers and organic crystals, chemical bonding between molecules is usually dominated by van der Waals interaction that can be easily modified by the pressure, up to 2 GPa (20 kbar) available to study ESR with a clamp-type pressure cell made of CuBe alloy. If pressure is applied to the conductive polymers, interchain coupling can be enhanced, giving rise to higher conductivity, reduced anisotropy, and possible phase transition of electronic and lattice states. In fullerides, such as alkali-C<sub>60</sub> compounds and TDAE-C<sub>60</sub>, their prominent physical properties, superconductivity, antiferromagnetism and ferromagnetism [24], will also be changed by the available pressure.



FIG. 7. Structure of SES. *s*-like electrons form a bcc lattice shown by the large spheres. The small balls represent the alkali atoms that surround an unpaired electron. Hexagons are actually flexible zigzag rings with six oxygen atoms. The lattice constant is 8.881 Å for SES and 9.247 Å for PES.

### 2. Alkali-Electro-Sodalite (AES)

Another example for the present pressure range is alkali-electro-sodalites ( $A_8$ (AlSiO<sub>4</sub>)<sub>6</sub>, AES). AES, shown in Fig. 7, is made of regularly alternating  $SiO_2$  and  $AlO_2$ networks, constructing a bcc structure of cages loaded with four alkali cations,  $A^+=Na^+$  or  $K^+$ , and one electron trapped by the cations, as a so-called F-center. Such a bcc lattice of s-electrons is known as a Mott-Hubbard insulator and has an antiferromagnetic ground state below  $\approx 50$  K for sodium-electro-sodalite (SES) and  $\approx 80$  K for the potassium analogue (PES) [25,26]. Although this system is composed of only strong covalent bonds, it is also known that AES will be compressed easily with the available pressure range because of the flexible bonding angle of Al-O-Si. Therefore, a Mott-Hubbard transition from an insulator to a metal might be realized by using pressure.



FIG. 8. The temperature dependence of the ESR integrated intensity in SES under ambient pressure,  $\approx 16$  and  $\approx 23$  kbar, estimated around 50 K [7].



FIG. 9. Pressure dependence of  $T_{\rm N}$  predicts  $T_{\rm N}$  goes to 0 K at  $\approx 70$  kbar. The solid curve is a guide for the eyes.

The integrated intensity of the ESR spectrum, which is proportional to the spin susceptibility, is plotted as a function of temperature in Fig. 8 [7]. The sharp decrease around 50 K at ambient pressure is an indication of a phase transition to an antiferromagnetic ground state. At the same time, an antiferromagnetic resonance (AFMR) should be growing below 50 K, but the observability of the AFMR depends on resonance positions and widths which are governed by the parameters of antiferromagnetism and the sample morphology. The resulting pressure dependence of the transition temperature is shown in Fig. 9 and suggests that  $T_{\rm N}$  approaches zero around 70 kbar.



FIG. 10. Schematic diagram of the Mott-Hubbard transition. t is the transfer integral, U the on-site Coulomb energy, AFI the antiferromagnetic insulator, and AFM the antiferromagnetic metal.

A naively expected response to the pressure is as follows: Since an overlap between neighboring electrons increases with decreasing lattice constant due to the pressure, the transfer energy t increases. Then, if the system is on the insulating side of the  $T_{\rm N}$  vs t/U diagram in Fig. 10,  $T_{\rm N}$  should increase with increasing pressure. With a small Curie-Weiss temperature of 250 K and an energy gap of 0.6 eV [27], it is probable for SES to be on the insulating side. This expectation contradicts the observed decrease of  $T_{\rm N}$  with pressure. The reason for this discrepancy could be accounted for by enhanced contraction of the hexagonal windows to connect neighboring electrons [7]. With increasing pressure, the bonding angle easily decreases, and three oxygens of the hexagonal window approach each other, giving rise to an increase in the potential barrier between the electrons.

# **IV. CONCLUSION**

In this report, it was demonstrated with examples of the conductive polymers and the sodium-electro-sodalite that ESR studies, especially as functions of frequency and/or pressure, can be powerful tools to investigate the electronic states in advanced materials.

#### ACKNOWLEDGMENTS

This work was partly supported by Grant-in-Aid for Scientific Research on the Priority Area "Fullerenes and Nanotubes" by the Ministry of Education, Science, Sports and Culture of Japan.

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