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Conduction-electron spin resonance in Langmuir-Blodgett films of a charge-transfer complex

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Electron-spin-resonance measurements were performed on the newly developed conducting Langmuir-Blodgett films consisting of a charge-transfer complex of bis(ethylenedioxy)tetrathiafulvalene (BO) and decyltetracyanoquinodimethane. The temperature-dependent spin susceptibility and linewidth clearly indicate that the major region of the films has a metallic nature. The density of states has been estimated as 3.5 states/eV per BO molecule, assuming no electron correlation. No metal-insulator transition has been detected at least down to 50 K, while an anomaly seen in the linewidth around 140 K suggests a certain kind of structural transition.

In recent years Langmuir-Blodgett (LB) films of charge-transfer (CT) complexes have attracted much interest as conducting ultrathin organic systems.[1] Nakamura *et al.*[2,3] obtained highly conducting LB films based on a newly developed amphiphilic CT complex of bis(ethylenedioxy)tetrathiafulvalene [Fig. 1(a), hereafter referred to as BO], which is the basis of various organic conductors[4,5] and several superconductors,[6,7] and decyltetracyanoquinodimethane [Fig. 2(b), C_{10}TCNQ]. The conductivity of these films reaches about 10 S/cm and exhibits metal-like temperature dependence ($\partial\sigma/\partial T < 0$) above 250 K.[2,3] To our knowledge, this system provides the first example of macroscopically metallic LB films without doping. The observed signs of the thermoelectric power[3] and the Hall resistance[8] indicate that the major charge carriers in the present system are holes. The charges on the BO and C_{10}TCNQ moieties in the major region (i.e., metallic region) were estimated as $+0.4$ and -1.0, respectively, from the IR spectra.[3] The macroscopic electric property of the films, however, may be strongly affected by the domain boundaries which may be associated with those seen in the atomic force microscope images. The activation-type temperature dependence of the conductivity observed at the lower temperatures was ascribed to the semiconducting nature of those domain boundaries. The observed thermoelectric power was interpreted by the linear combination of the components due to metallic and semiconducting regions. Therefore, microscopic evidence for the existence of conduction electrons in these newly developed LB films is needed to clarify the metallic nature of the system. Such evidence can be provided by the characterization of the metallic region using the electron spin resonance (ESR) spectroscopy.[9,10]

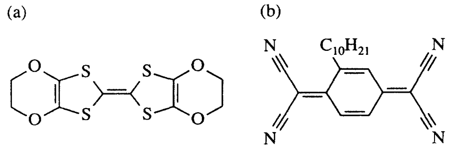

FIG. 1. Chemical structure of (a) BO and (b) C_{10}TCNQ.

In this paper we report a clear observation of the Pauli susceptibility in a wide temperature range in the CT-complex LB films. The ESR measurements were performed on the BO-C_{10}TCNQ LB films and two spin species were observed: species *A* and *B* are the major- and minor-spin species, respectively The metallic nature of the major region of the films has been shown by the temperature dependence of the spin susceptibility and the linewidth of species *A*. The density of states has been estimated as 3.5 states/eV per BO molecule in the temperatures range of 50–294 K from the obtained Pauli susceptibility, ignoring the electron correlation. The dominant contribution of the Elliott mechanism,[11] which is the major-spin relaxation mechanism in normal metals, to the linewidth has been suggested. Further, no metal-insulator transition has been detected at least down to 50

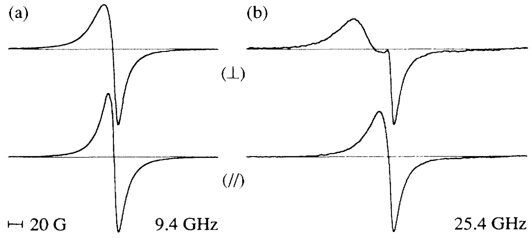

FIG. 2. The ESR spectra of a BO-C_{10}TCNQ LB film at room temperature with the external magnetic field perpendicular (⊥) and parallel (‖) to the film plane observed at the (a) *X* and (b) *K* bands. The microwave power applied is less than 12.5 mW.

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K, although a certain kind of structural transition around 140 K has been suggested by the anomaly seen in the linewidth.

LB samples were obtained by the horizontal lifting method from the mixed monolayer of the BO-C_{10}TCNQ complex (BO:C_{10}TCNQ:H_2O=10:4:1) and icosanoic acid on pure water spread from a benzene-acetonitrile solution.[2,3] The molar ratio of C_{10}TCNQ and icosanoic acid in the solution was 1:1. The samples consisted of 20–60 monolayers on sheets of polyethylene terephthalate[12] (0.1 mm thick) precoated with five layers of cadmium icosanate. ESR measurements were performed using a Bruker ESP-300E spectrometer equipped with an Oxford ESR900 cryostat at the X band (9.4 GHz) and a conventional homodyne spectrometer at the K band (25.4 GHz).

The ESR spectra of a BO-C_{10}TCNQ LB film at 294 K with the external magnetic field perpendicular ($\perp$) and parallel ($\|$) to the film plane observed at the X and K bands are shown in Figs. 2(a) and 2(b), respectively. The clear anisotropy due to orientational order is observed as expected for the LB films.[13,14] The structure due to the g-value difference, which is expanded at the K band, can be seen in the spectra. The saturation measurements at the X band indicate that the spin-lattice-relaxation time of the larger g-value component (hereafter denoted as species A) is shorter than that of the smaller g-value component (species B). Species A has broader linewidth. The line shapes of both species are nearly of Lorentzian in the ($\|$) direction. Therefore, the spectra with this direction were decomposed by using the least-square-fitting method assuming Lorentzian line shapes [Fig. 3(a)]. Line shapes compatible with these fitting results can be also obtained by subtracting the spectra recorded at different microwave powers when the normalization factor was appropriately adjusted [Fig. 3(b)]. The estimated spin numbers of species A and B are about 0.09 and 0.01 spin/BO molecule, respectively, at 294 K.

The temperature-dependent spin susceptibility (χ_s) obtained from the numerical integration of the observed ESR spectrum is shown by the filled circles in Fig. 4. The open triangles and squares in this figure represent the components due to the spin species A and B, respectively, estimated from the fitting results. In this paper we would like to restrict our attention to the temperature range above 50 K, because below that temperature species A, the major-spin species, shows Curie-like susceptibility (Fig. 4, inset) possibly due to disorders. It should be noted here, however, that the observed Curie-like component is smaller than those in the CT-complex LB films of one-dimensional (1D) nature,[14–16] suggesting higher dimensionality of the present system.[9] The temperature dependence of the full width at half maximum $\Delta H_{1/2}$ of the observed spectrum in the integrated form is shown by the filled circles in Fig. 5. $\Delta H_{1/2}$ of species A and B estimated from the fitting results are also shown in this figure by the open triangles and squares, respectively.

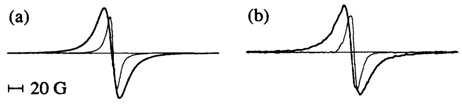

FIG. 3. (a) The decomposed line shapes for species A (thick lines) and B (thin lines) in the ($\|$) direction at the X band obtained by using the least-square-fitting method assuming Lorentzian line shapes. (b) The subtraction of the spectrum recorded at 200 (12.5) mW from that recorded at 12.5 (200) mW with an adjusted normalization factor gives the line shape of species A (B) compatible with the fitting result.

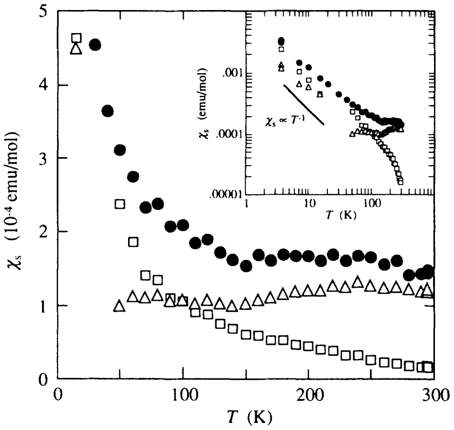

FIG. 4. The filled circles represent the temperature-dependent spin susceptibility of a BO-C_{10}TCNQ LB film obtained from the numerical integration of the observed ESR spectrum. The susceptibility components due to the spin species A and B, respectively, estimated by the least-square-fitting method are shown by the open triangles and squares. The value corresponds to the susceptibility per 1 mole of the BO molecules. It should be mentioned that the spectra around 30 K were not successfully decomposed, since the g values and linewidths of both species are close to each other in the ($\|$) direction at this temperature range.

The temperature dependence of χ_s (Fig. 4) and $\Delta H_{1/2}$ (Fig. 5) of species A indicates the conduction electron nature of this species, according to the following discussion. The approximately constant χ_s of species A above 50 K may be attributed to a Pauli susceptibility of conduction electrons or to a susceptibility of low-dimensional antiferromagnets with the exchange integral of 200–300 K. The latter possibility, however, can be eliminated by the temperature dependence of $\Delta H_{1/2}$ (decreasing as the temperature is lowered), since the linewidth of the low-dimensional antiferromagnets should show a prominent increase in the lower temperature range due to the development of the short-range order.[17,18] The obtained susceptibility of about 1.2×10^{-4} emu/mol of BO molecules (3×10^{-4} emu/mol of charge carriers) is close to the reported value for the crystals of other BO complexes.[4,5]

The dominant contribution of the BO spins to species A is suggested by the estimated g value of this species in the temperature range of 50–294 K: about 2.004 and 2.008 for ($\|$) and ($\perp$) directions, respectively. These values are larger than the reported g value of the TCNQ spins (2.003) (Ref. 14) and close to the g value of the BO- (Ref. 5) and (BEDT-TTF)-complex crystals,[19,20] where BEDT-TTF is an analogous compound of BO. This result is consistent with the thermoelectric power and the

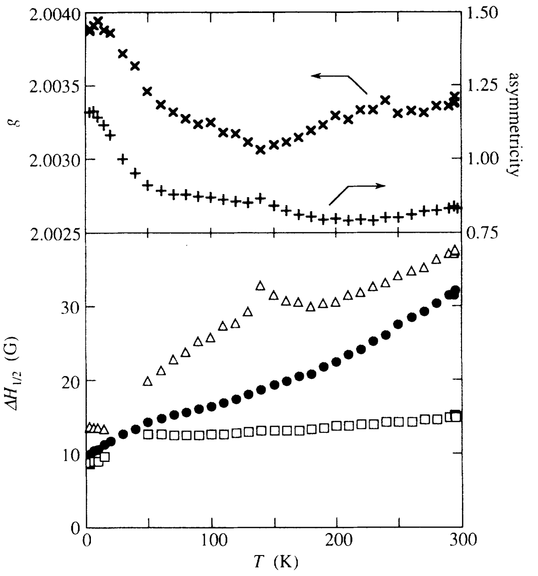

FIG. 5. The filled circles stand for the temperature dependence of the full width at half maximum of the observed spectrum in the integrated form. Those of the decomposed lines of the spin species A and B are represented by the open triangles and squares, respectively. The g value at the peak of the observed integrated spectrum is shown by ×. The ratio of the maximum and minimum peak heights of the observed derivative spectrum is indicated by +. The external magnetic field is parallel to the film plane.

Hall measurements, which showed that the conduction electrons are located on the BO stacks. On the contrary, the possible contribution of the TCNQ spins to species A may be insignificant. Since the Hubbard or Peierls-Hubbard model can be applied to the TCNQ$^-$ stacks, they may be in the 1D antiferromagnetic state or spin Peierls state. The dominant contribution of antiferromagnetically coupled or thermally excited spins in species A can be denied as already discussed.

Based on the above arguments, the density of states $D(\varepsilon_F)$ can be estimated as 3.5 states/eV per BO molecule using χ_s value at room temperature, by assuming the normal Pauli susceptibility, $\chi_s = \mu_B^2 D(\varepsilon_F)$, for the present system. It should be noted that the obtained value may be the upper limit, because we neglected the possible enhancement of χ_s caused by the electron correlation.[21] The weak temperature dependence of χ_s (Fig. 4, △) shows that no metal-insulator transition occurs in the metallic region at least down to 50 K, although it may reflect the change in $D(\varepsilon_F)$ due to the possible temperature variation of the lattice constants. This result and the relatively small Curie component, which is seen below 50 K, suggest higher dimensionality of the electronic system in the present films compared with, e.g., the TMTTF-C_{14}TCNQ LB films of 1D nature.[16]

The estimated $\Delta H_{1/2}$ of species A decreases almost linearly as the temperature is lowered except for the anomaly around 140 K (Fig. 5). This behavior is consistent with the Elliot mechanism,[11] which entails a linewidth proportional to the temperature above the Debye temperature[22] considering the weak temperature dependence of the g value and $D(\varepsilon_F)$ above 50 K. Further, the anisotropy of $\Delta H_{1/2}$ is qualitatively consistent with the Elliot mechanism, i.e., the larger $\Delta H_{1/2}$ is obtained for the direction with the larger g value (see Fig. 2). It should be noted, however, that the finite linewidth at very low temperatures indicates considerable contributions of other mechanisms such as a defect-related one. The linewidth decreasing with decreasing temperature is already reported for the crystals of other BO complexes, but it tends to zero in those cases.[4,5]

The g value and the asymmetricity of the observed spectrum show a minimum and a maximum around 140 K, respectively (Fig. 5). This anomaly corresponds to the maximum of $\Delta H_{1/2}$ of species A. Since no distinct change in $D(\varepsilon_F)$ is observed around 140 K, and since $\Delta H_{1/2}$ is considered to be governed by the Elliott mechanism, this increase in the spin-relaxation rate suggests some structural fluctuations occurring outside the conducting columns in the metallic region. The onset of this increase in the electron scattering rate around 180 K may be related with the reported change in the temperature dependence of the thermoelectric power.[3] The possible phase transitions concerning the ethylene groups[23] in the BO molecules, the TCNQ stacks, and the alkyl chains are candidates of the origin of this anomaly.

The estimated g value of species B is about 2.003 in the temperature range of 50–294 K, implying the dominance of the TCNQ spins in this species. The Curie-like susceptibility (Fig. 4) and the approximately constant linewidth (Fig. 5) suggest that species B consists of weakly interacting spins. It should be pointed that the transportational and spin degrees of freedom are decoupled in the 1D Hubbard system when the population of the doubly occupied sites is low due to the large on-site Coulomb interaction.[24] In other words, electrons in such a system may be able to show both Curie-like susceptibility and activation-type conductivity. Thus we would like to note the possibility that species B is located in the semiconducting region, whose constituents are suggested to be chemically different from those of the metallic region.[3]

From these results, it is concluded that the BO-C_{10}TCNQ LB films contain the metallic region. Although the detailed mechanism of the structural transition suggested by the linewidth anomaly is not clear at present, further studies of the present films, having a unique structure due to the presence of alkyl chains, may provide new insights into the electronic properties of BO-related materials.

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[1] See, for example, Proceedings of the 6th International Conference on Organized Molecular Films, Trois-Rivière, Canada, 1993 [Thin Solid Films (to be published)].

[2] T. Nakamura, G. Yunome, R. Azumi, M. Yumura, M. Matsumoto, S. Horiuchi, H. Yamochi, and G. Saito, Synth. Met. **55-57**, 3853 (1993).

[3] T. Nakamura, G. Yunome, R. Azumi, M. Tanaka, H. Tachibana, M. Matsumoto, S. Horiuchi, H. Yamochi, and G. Saito, J.

Phys. Chem. **98**, 1882 (1994).

[4] T. Suzuki, H. Yamochi, H. Isotaro, C. Fite, H. Kasmai, K. Liou, G. Srdanov, F. Wudl, P. Coppens, K. Maly, and A. Frost-Jansen, Synth. Met. **41-43**, 2225 (1991).

[5] H. Yamochi, S. Horiuchi, G. Saito, M. Kusunoki, K. Sakaguchi, T. Kikuchi, and S. Sato, Synth. Met. **55-57**, 2096 (1993).

[6] M. A. Beno, H. H. Wang, A. M. Kini, K. D. Carlson, U. Geiser, W. K. Kwok, J. E. Thompson, J. M. Williams, J. Ren, and M.-H. Whangbo, Inorg. Chem. **29**, 1599 (1990).

[7] S. Kahlich, D. Sweitzer, I. Heinen, S. E. Lan, B. Nuber, H. J. Keller, K. Winzer, and H. W. Helberg, Solid State Commun. **80**, 191 (1991).

[8] M. Takenaga, A. Abdulla, A. Kasai, A. Nakamura, T. Nakamura, M. Matsumoto, S. Horiuchi, H. Yamochi, and G. Saito, Appl. Phys. Lett. (to be published).

[9] S. Kuroda, K. Ikegami, and M. Sugi, Mol. Cryst. Liq. Cryst. **190**, 111 (1990).

[10] S. Kuroda, Colloids Surf. A **72**, 127 (1993).

[11] R. J. Elliott, Phys. Rev. **96**, 266 (1954).

[12] S. Kuroda, M. Sugi, and S. Iizima, Thin Solid Films **99**, 21 (1983).

[13] K. Ikegami, S. Kuroda, Y. Tabe, K. Saito, M. Sugi, M. Matsumoto, T. Nakamura, and Y. Kawabata, Jpn. J. Appl. Phys. **31**, 1206 (1992).

[14] K. Ikegami, S. Kuroda, M. Sugi, T. Nakamura, H. Tachibana, M. Matsumoto, and Y. Kawabata, J. Phys. Soc. Jpn. **61**, 3752 (1992).

[15] K. Ikegami, S. Kuroda, M. Saito, K. Saito, M. Sugi, T. Nakamura, M. Matsumoto, and Y. Kawabata, Phys. Rev. B **35**, 3667 (1987).

[16] K. Ikegami, S. Kuroda, K. Saito, M. Saito, M. Sugi, T. Nakamura, M. Matsumoto, Y. Kawabata, and G. Saito, Synth. Met. **27**, B587 (1988).

[17] P. M. Richards and M. B. Salamon, Phys. Rev. B **9**, 32 (1974).

[18] Y. Tazuke and K. Nagata, J. Phys. Soc. Jpn. **38**, 1003 (1975).

[19] N. Kinoshita, M. Tokumoto, H. Anzai, and G. Saito, J. Phys. Soc. Jpn. **54**, 4498 (1985).

[20] T. Sugano, G. Saito, and M. Kinoshita, Phys. Rev. B **34**, 117 (1986).

[21] J. B. Torrance, Y. Tomkiewicz, and B. D. Silverman, Phys. Rev. B **15**, 4738 (1977).

[22] Y. Yaffet, Solid State Phys. **14**, 1 (1963).

[23] M. Tokumoto, N. Kinoshita, K. Murata, H. Bando, and H. Anzai, in *Advanced Organic Solid State Materials,* edited by L. Y. Chiang, P. Chaikin, and D. O. Cowan, MRS Symposia Proceedings No. 173 (Materials Research Society, Pittsburgh, 1990), p. 107.

[24] J. B. Sokoloff, Phys. Rev. B **2**, 779 (1970).