

Random-exchange Heisenberg antiferromagnetic chains in Langmuir-Blodgett films of *N*-docosylpyridinium-bistetracyanoquinodimethane

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An ESR investigation is performed on Langmuir-Blodgett (LB) films consisting of a surface-active 1:2 complex of *N*-docosylpyridinium and tetracyanoquinodimethane (TCNQ). A characteristic temperature dependence in the spin susceptibility and the linewidth is observed, which shows reasonable agreement with the random-exchange Heisenberg antiferromagnetic chain (REHAC) model of Soos and Bondeson.

The Langmuir-Blodgett (LB) technique¹ has attracted much attention as a tool for constructing monolayer assemblies with specific structures using various constituent materials.² It is important to understand the extent to which the physical properties of the constituents are modified in LB films as compared with those of the corresponding crystalline systems. Recently LB films with three types of surface-active charge-transfer complexes have been generated: *I*₂-doped *N*-docosylpyridinium-tetracyanoquinodimethane-(TCNQ),^{3,4} *N*-docosylpyridinium-(TCNQ)₂,⁵ and tetramethyltetrathiafulvalene (TMTTF)-octadecylTCNQ.⁶ The magnetic properties of *N*-docosylpyridinium-(TCNQ)₂ [Fig. 1, hereafter referred to as C₂₂Py(TCNQ)₂], one of the 1:2 complexes of TCNQ, is of particular interest. Magnetic properties of crystalline samples of 1:2 complexes of TCNQ are classified into either regular antiferromagnetic systems⁷ or random-exchange Heisenberg antiferromagnetic chain (REHAC) systems.⁸⁻¹⁰

We have measured the spin susceptibility of the LB films and powders of C₂₂Py(TCNQ)₂ using an ESR technique. The observed behavior is adequately explained by the REHAC model. In addition, the occurrence of the alternate exchange interactions¹¹ is suggested for powder samples of the same complex.

The Hamiltonian of the REHAC system is given as

$$\mathcal{H} = \sum_n 2X_n JS_n \cdot S_{n+1} - g\mu_B H \sum_n S_n^z, \quad (1)$$

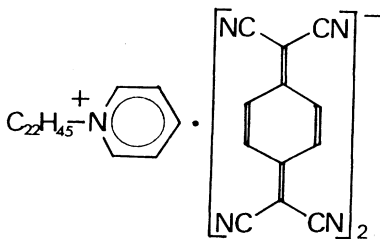


FIG. 1. Chemical structure of *N*-docosylpyridinium-(TCNQ)₂.

where *J* is the exchange integral in ideal antiferromagnetic chains. *X_n* (0 ≤ *X_n* ≤ 1) are random variables, representing the disorder. The behavior of the system is determined by choosing a proper form of the distribution function *f*(*X*) for *X_n*. Soos and Bondeson^{9,10} showed that the normalized bimodal distribution

$$f(X) = c\delta(\epsilon - X) + (1 - c)\delta(1 - X) \quad (2)$$

is the simplest choice for reproducing the spin susceptibility of quinolinium-(TCNQ)₂ and acridinium-(TCNQ)₂ for the whole temperature range, where *c* and (1 - *c*) are the concentrations of weak exchanges ϵJ and strong exchanges *J* along the chains, respectively. The calculated susceptibility shows a clear crossover. For higher temperatures of $k_B T > \epsilon J$, the magnetic chains are decoupled into segments due to the weak (ϵJ) exchange linkages. Each segment consists of either even or odd numbers of spins. In this limit the behavior of χ is determined by short-range order in the finite-length segments and is characterized by a broad peak centered around $k_B T = 1.2 J$, as for the Bonner-Fisher susceptibility of a regular antiferromagnetic chain χ_B .¹² As the temperature is lowered, even- and odd-length segments are frozen into their ground states, singlet and doublet, respectively. A crossover takes place around the temperature given below,

$$\chi_B(T)/\chi_c \approx c/(2 - c), \quad (3)$$

where $\chi_c = Ng^2\mu_B^2 S(S+1)/3k_B T$ is the susceptibility of free spins and $c/(2 - c)$ is the probability for odd segments. Below this temperature the susceptibility χ obeys a $T^{-\alpha}$ (0 ≤ α ≤ 1) law. This behavior results from the weak interactions between odd-length segments. We note that the above situation cannot arise in two- or three-dimensional magnets, where the effect of the disorder on the spin correlation is much less significant than in the one-dimensional case.⁸

In the following, it is shown that the observed temperature dependence of the ESR signal in the powder and LB films of C₂₂Py(TCNQ)₂ is consistent with the REHAC model.

Samples were prepared by the standard vertical dipping

method.¹³ The preparation conditions were the same as those described previously.⁵ The samples consist of 1 to 15 layers of $C_{22}Py(TCNQ)_2$ as Z-type film on sheets of polyethylene terephthalate (0.1 mm thick) coated with multilayers of cadmium arachidate. ESR measurements were performed using a Varian E-4 spectrometer in the temperature range of 4–300 K. Measurements were also made on a powder sample of $C_{22}Py(TCNQ)_2$ for comparison. The absolute magnitude of the spin susceptibility was calibrated using crystals of $CuSO_4 \cdot 5H_2O$ as a standard. For the powder sample, the static susceptibility was also measured using the Faraday method.

The ESR absorption of LB films of $C_{22}Py(TCNQ)_2$ was nearly of Lorentzian line shape. The g value was around 2.003. The spin density of the system at 300 K was estimated to be 0.3 ± 0.1 spins/complex.

The filled circles in Fig. 2 show the temperature dependence of the normalized spin susceptibility χ/χ_c , where χ_c is obtained using the total number of $(TCNQ)_2^-$. This quantity gives the effective number of spins at any temperature. The observed χ/χ_c is independent of temperature below 100 K, but it tends to increase in the higher-temperature region. As is discussed below, this behavior is consistent with the REHAC model in the limit of completely decoupled chains [$\varepsilon=0$ in Eq. (2)].

The present LB films are low-dimensional systems, where each active layer consists of $(TCNQ)_2^-$ which is

separated from its neighbors by inert layers of long alkyl chains. The ESR signals observed in monolayered samples and multilayered samples were identical, and this fact shows that the interlayer interactions between magnetic moments are negligible. Therefore, the magnetic moments of $(TCNQ)_2^-$ should form a low-dimensional magnetic system. In this case, the decrease in the spin susceptibility with temperature from 300 down to 100 K corresponds to the onset of antiferromagnetic short-range order between magnetic moments. However, unlike the ideal low-dimensional system without disorder, the spin susceptibility shows a Curie-like behavior at low temperatures, which can originate from either a random-exchange interaction^{9,10} or isolated spins such as those trapped at grain boundaries. It was found, however, that the present data cannot be reproduced by a linear combination of the susceptibilities from regular one-dimensional chains¹² and free spins. A similar discussion may be extended to the two-dimensional case.

Therefore, the low-temperature behavior of χ/χ_c is ascribed to the presence of random-exchange interactions in the antiferromagnetic chain. As discussed above, the higher-temperature behavior is approximated by the Bonner-Fisher curve in the REHAC model of Soos and Bondeson. The solid line in Fig. 2 is the Bonner-Fisher curve $\chi_B(T)$ for $J=320$ K. The broad maximum of the spin susceptibility expected for $\chi_B(T)$ could not be observed because of the thermal instability of the samples. The constant χ/χ_c ($\alpha \approx 1$) below 100 K, corresponds to the limiting case of complete decoupling of the chain ($\varepsilon=0$). Using Eq. (3), we obtain $c \approx 0.2$, which reflects a higher degree of disorder inherent in LB films.

The behavior of REHAC is typically observed on the powder of $C_{22}Py(TCNQ)_2$ in the lower-temperature range. The susceptibility increases as $T^{-\alpha}$ ($\alpha=0.7$) below 100 K, as shown by the open circles in Fig. 2. The lower value of α compared to the LB film case may be ascribed to the lower degree of disorder. The higher-temperature behavior, however, deviates from the Bonner-Fisher curve, decreasing more steeply as the temperature is lowered. This discrepancy is partly removed by assuming the occurrence of alternate exchange interactions,¹¹ which produce steeper susceptibility decrease as compared with the case of the uniform chain. The dotted lines in Fig. 2 show a theoretical curve of an alternating chain with $J_1=600$ K and $J_2/J_1=0.4$. There still remains, however, a discrepancy, which is more clearly seen in the linear plot of $\chi(T)$ shown by the inset of Fig. 2. The effect of random exchange increases the susceptibility compared with that for the regular chain,¹⁰ which may explain the remaining discrepancy. Another possible explanation for the difference between the observed and theoretical curves could be a temperature dependence of J_2/J_1 , which was proposed to interpret a similar steep variation of $\chi(T)$ in a cyanine dye- $(TCNQ)_2$ single crystal.¹⁴ The REHAC with alternate exchange interactions has already been predicted by Bondeson and Soos.¹⁰ It should be mentioned that we cannot exclude the possibility of alternate exchange interactions in LB films because of the small difference between the theoretical curves of the regular antiferromagnetic chains and alternate exchange antiferro-

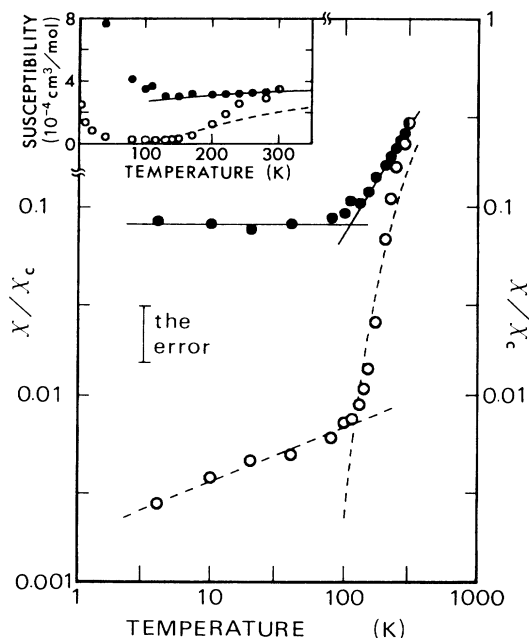


FIG. 2. Temperature dependence of the normalized spin susceptibility of an LB film (●) and that of a powder sample (○). The solid line of the higher-temperature side is the theoretical curve for the regular antiferromagnetic chain with $J=320$ K according to Bonner and Fisher (Ref. 12). The dotted line of the higher-temperature side is the theoretical curve for the alternating chain (Ref. 11) with $J_1=600$ K and $J_2/J_1=0.4$. The solid and dotted lines of the lower-temperature side refer to power laws of $\chi \propto T^{-1}$ and $\chi \propto T^{-0.7}$, respectively.

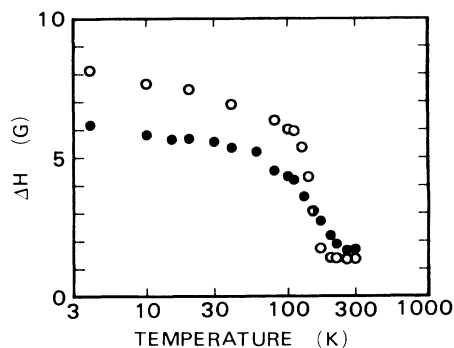


FIG. 3. Temperature dependence of the full width at half maximum ΔH of the ESR signal observed in an LB film (●: the external magnetic field is perpendicular to the film) and that observed in a powder sample (○).

magnetic chains with J_2/J_1 close to 1 in the higher-temperature range shown in Fig. 2.

While there is some complication in the high-temperature behavior of the susceptibility, as discussed above, the temperature dependence of the ESR linewidth in the low-temperature range further suggests that the REHAC system is realized in the powder sample. The REHAC model predicts that the full width at half maximum of the exchange-narrowed ESR signal ΔH should be proportional to $\ln(T_0/T)$ in the low-temperature range¹⁵ (T_0 is a constant). This results primarily from the temperature dependence of the effective exchange interaction between frozen odd segments. The temperature dependence of ΔH , shown by the open circles in Fig. 3, is compatible with the REHAC model up to about 100 K. It is noted here that the crossover point of the susceptibility from the higher-temperature regime to the lower-temperature regime is around 100 K, which is in remarkable agreement with the linewidth variations. In the limit of completely decoupled chains ($\epsilon=0$), as suggested to be the case with the LB films, the characteristic temperature dependence of the effective intrachain exchange interaction, which arises through the weak exchange ϵJ , would not be expected. The actual variation of ΔH for LB films (filled circles in Fig. 3) shows a weak but similar temperature dependence for the powders. The crossover of the linewidth from the low-temperature regime to the high-temperature regime around 80 K also coincides with that of the susceptibility. These observations may suggest that the system has small but finite ϵ , or that there are some distributions of the value of ϵ .

The ΔH anisotropy of the LB system at 300 and 4 K are shown in Fig. 4. The minimum of the linewidth is located between $\theta=35^\circ$ and 55° (θ is the angle between the magnetic field and the plane normal). The position of the ob-

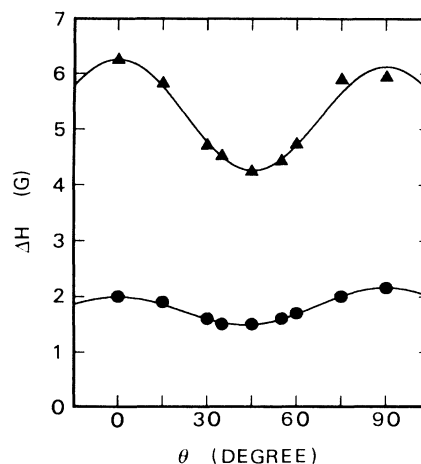


FIG. 4. Anisotropy of the ESR linewidth observed in an LB film at 300 K (●) and 4 K (▲). The solid lines are to guide the eye.

served minimum at 300 K is reasonably explained by the characteristic angular dependence of ΔH of one-dimensional chains¹⁶ (i.e., a minimum ΔH at a magic angle) assuming a random distribution of the chain axis in the film plane. The similar angular dependence at 4 K indicates that the linewidth is governed by the dipolar interactions between frozen segments. Further discussion of the linewidth anisotropy is beyond the scope of this paper.

The results mentioned above indicate the development of the one-dimensional chains of $C_{22}Py(TCNQ)_2$ in the LB films, whereas *N*-methylpyridinium-(TCNQ)₂ and its derivatives, which are not associated with long alkyl chains, behave as two- or three-dimensional antiferromagnetic systems.⁷ Therefore the presence of long alkyl chains has resulted in the occurrence of REHAC with alternate exchange in powders, a characteristic feature which is also reflected in the more disordered LB system. This represents a significant modification of physical properties. Moreover, we note the possibility of controlling the degree of disorder introduced into the system by changing the preparation conditions and/or employing a second treatment after deposition.

In conclusion, we have described an ESR study on LB films and powders of *N*-docosylpyridinium-(TCNQ)₂. The observed magnetic properties can be understood as those of REHAC systems.

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