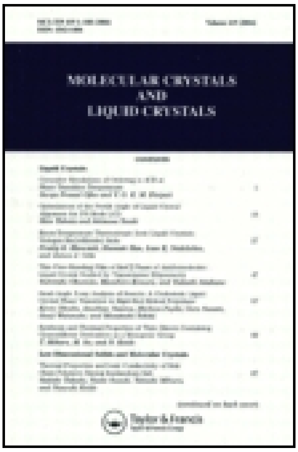

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ORGANIC FERROMAGNETISM OF THE QUASI-TWO-DIMENSIONAL HYDROCARBON

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Abstract A new quasi-two-dimensional hydrocarbon is proposed as a model of organic ferromagnets. This compound is the carbon-atom network bridged by carbon atoms. The itinerant π electrons interact through the Coulomb repulsion on the same carbon atom of network and bridging sites. The π electron at bridging carbon atom couples the nonbonding-localized elecron through the ferromagnetic-exchange interaction. This π-electron system is studied by a Kondo-Hubbard model within the mean-field theory using the periodic-boundary condition. The total energy, the energy bands, and the spin densities have been computed. It turns out that the ferromagnetic ground state is stabilized than the nonmagnetic one through the ferromagnetic-exchange interaction, the antiferromagnetic correlation, and the topological structure of this compound.

INTRODUCTION

Many researchers have made every efforts to obtain organic ferromagnets of compounds not including d and f electorns but s and p electrons. For the sake of studies on organic ferromagnetism, hydrocarbons have been experimentally[1,2] and theoretically[3,4] studied. Theoretically, Nasu[5] proved ferromagnetism of a quasi-one-dimensional (Q1D) m-polydiphenylcarbene and we[6,7] examined the effects of next-nearest-neighbor-site transfer integral and nearest-neighbor-site Coulomb interaction on that. We proposed ferromagnetism of a new 3D carbon network,[8] because a long-range magnetic order does not appear in pure 1D and 2D systems.[9]

In this paper, the electronic and magnetic properties of a new quasi-two-dimensional (Q2D) hydrocarbon are studied. This compound is the carbon-atom network bridged by a single carbon atom with a π electron and a nonbonding-localized one. The π electrons on the carbon-atom network and the bridging-carbon atoms are itinerant and interact mutually through the antiferromagnetic correlation. The π eletron at bridging-carbon atom couples the nonbonding electron through the ferromagnetic-exchange interaction. The Kondo-Hubbard model for this π-electron system is investigated within the mean-field theory with the periodic boundary condition. The total energy per electron, the energy bands, and the spin densities are computed. The purpose of this work is to elucidate that the on-site Coulomb and ferromagnetic-exchange interactions of itinerant π electrons lead to ferromagnetism due to the topological structure in this system. The interlayer interaction will be considered in future.

THE Q2D HYDROCARBON AND A KONDO-HUBBARD MODEL

Let us consider the Q2D hydrocarbon as illustrated in Figure 1. This compound is the carbon-atom network bridged by carbon atoms. The unit cell is composed of a bridging-carbon atom ($m = 1$) and ten carbon atoms ($m = 2 \sim 11$). A π electron per carbon atom moves itinerantly between nearest-neighbor carbon atoms through the transfer energy t. The π electron and the nonbonding one at bridging-carbon atom interact through the ferromagnetic-exchange energy J.

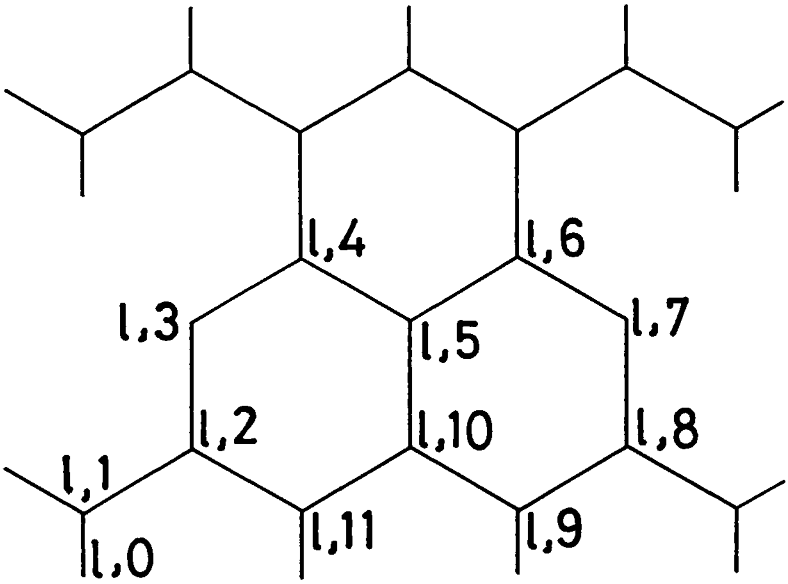

FIGURE 1 Carbon-atom network of the quasi-two-dimensional hydroncarbon. l denotes the l-th unit cell, $1 \sim 11$ the carbon-atom site, and 0 the nonbonding-localized-electron site.

The Hamiltonian for this π-electron system is written as

$$H = H_0 + H_1, \tag{1}$$

where

$$H_0 = -t\sum_{l,\sigma}(\sum_{m=1}^{10} a^\dagger_{lm\sigma}a_{l,m+1,\sigma} + a^\dagger_{l2\sigma}a_{l11\sigma} + a^\dagger_{l5\sigma}a_{l10\sigma}$$
$$+a^\dagger_{l8\sigma}a_{l+l_a,1\sigma} + a^\dagger_{l4\sigma}a_{l+l_b,11\sigma} + a^\dagger_{l6\sigma}a_{l+l_b,9\sigma} + \mathrm{H.c.}) \tag{2}$$

and

$$H_1 = U\sum_l \sum_{m=1}^{11} n_{lm\alpha}n_{lm\beta} - J\sum_l \mathbf{S}_{l0}\cdot\mathbf{S}_{l1}, \tag{3}$$

where $a^\dagger_{lm\sigma}$ ($a_{lm\sigma}$) is the creation (annihilation) operator for an electron of spin σ (α (β) denotes up (down) spin) at site m (the distance between nearest-neighbor sites is 1) in the l-th unit cell, $l = (n_1, n_2)$, where n_1 and n_2 are arbitrary integers, $l_a = (1,0)$, $l_b = (0,1)$. The $n_{lm\sigma} = a^\dagger_{lm\sigma}a_{lm\sigma}$ is the number operator and $\mathbf{S}_{l1}$ ($\mathbf{S}_{l0}$) is the spin operator of the π (nonbonding) electron at bridging-carbon atom.

MEAN-FIELD THEORY

We use the mean-field theory to see the stabilization of the ferromagnetic state for the finite U and J. We assume that the system has six up- and five down-spin π electrons and a nonbonding electron in the unit cell in the ground state.

$$\sum_{m=1}^{11} < n_{lm\alpha} >= 6, \sum_{m=1}^{11} < n_{lm\beta} >= 5, < S^z_{l0} >= 1/2, \tag{4}$$

where $< \cdots >$ denotes the ground-state average. This state should be determined self-consistently within the mean-field theory. S^z_{l0} is the z component of $\mathbf{S}_{l0}$. We set $\hbar = 1$. We also assume the neutrality of the carbon atom

$$\sum_\sigma < n_{lm\sigma} >= 1 \tag{5}$$

and define a half of the spin density

$$\delta n_m =< n_{lm\alpha} - n_{lm\beta} > /2. \tag{6}$$

To make the Hamiltonians of up- and down-spin electrons symmetric, we use the following transformations:

$$a_{lm\alpha} \rightarrow b_{lm\alpha}, a_{lm\beta} \rightarrow (-1)^{m+1}b^\dagger_{lm\beta}. \tag{7}$$

We get

$$\sum_{m=1}^{11} < b^\dagger_{lm\sigma}b_{lm\sigma} >= 6 \tag{8}$$

and

$$< H/t >= \sum_{\mathbf{k},\sigma} \mathbf{b}^{\dagger}_{\mathbf{k}\sigma} M(\mathbf{k}) \mathbf{b}_{\mathbf{k}\sigma} + NU \sum_{m=1}^{11} \delta n_m^2/t + N(13U+J)/4t, \tag{9}$$

where the sum of wave vector is taken under the conditions

$$0 \le k_x \le \sqrt{3}\pi/3, 0 \le k_y \le \pi, \tag{10}$$

$\mathbf{b}^{\dagger}_{\mathbf{k}\sigma}$ is a 11D low vector

$$\mathbf{b}^{\dagger}_{\mathbf{k}\sigma} = [b^{\dagger}_{\mathbf{k}1\sigma}, \cdots, b^{\dagger}_{\mathbf{k}11\sigma}] \tag{11}$$

with the Fourier transform of $b^{\dagger}_{lm\sigma}$,

$$b^{\dagger}_{\mathbf{k}m\sigma} = \sum_l \exp(i\mathbf{k}\cdot\mathbf{r}_l) b^{\dagger}_{lm\sigma}/\sqrt{N}, \tag{12}$$

N is the total number of unit cells and $M(\mathbf{k})$ is a 11 × 11 Hermite matrix. Its elements are $M_{1,1} = -U\delta n_1/t - J/4t, M_{m,m} = -U\delta n_m/t (m = 2 \sim 11), M_{m,m+1} = M_{m+1,m} (m = 1 \sim 10) = M_{2,11} = M_{11,2} = M_{5,10} = M_{10,5} = -1, M_{1,8} = M^*_{8,1} = -\exp(-i\sqrt{3}k_x), M_{4,11} = M_{6,9} = M^*_{11,4} = M^*_{9,6} = -\exp(-ik_y)$, and other elements are 0.

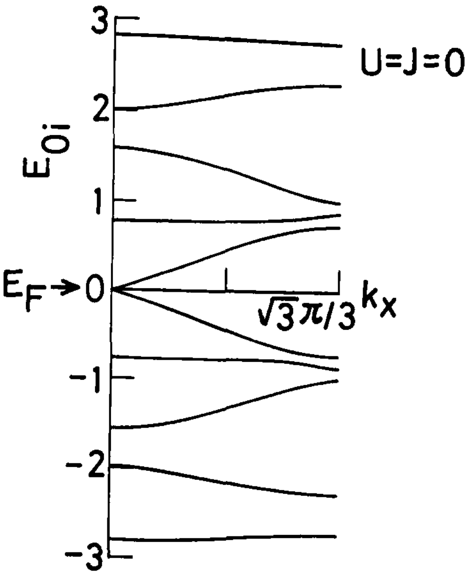

FIGURE 2 Eleven energy bands of π electrons along the direction of k_x axis for $U = J = 0$. E_{0i}, E_F, and k_x denote the energy reduced by t, the Fermi energy, and the wave vector, respectively.

From the eigenvalue equation

$$M(\mathbf{k})\mathbf{V}_i(\mathbf{k}) = E_i(\mathbf{k})\mathbf{V}_i(\mathbf{k}), (i = 1 \sim 11), \tag{13}$$

we get the eigenvalue $E_i(\mathbf{k})$ and the eigenvector $\mathbf{V}_i(\mathbf{k})$ of $M(\mathbf{k})$. Using $\mathbf{V}_i(\mathbf{k})$, Equation (6) becomes

$$\delta n_m = \sum_{\mathbf{k}} \sum_{i=1}^{6} V^*_{m,i}(\mathbf{k}) V_{m,i}(\mathbf{k})/N - 1/2, \tag{14}$$

where the component $V_{m,i}(\mathbf{k})$ of $\mathbf{V}_i(\mathbf{k})$ denotes the amplitude at site m.

Using Eq. (13), we get eleven energy bands of π electrons for $U = J = 0$, and they are shown along the directions of k_x and k_y axes in Figures 2 and 3, respectively. We have five bands having negative energies, those having positive energies, and a band at zero energy. The first and second come from ten π electrons on the carbon-atom network and the third the π electron at bridging-carbon atom. We get 2^N degenerate ground states. We can get a ferromagnetic state, when the localized band is occupied only by up-spin electrons due to the topological structure, the ferromagnetic-exchange interaction, and the Coulomb-repulsive interaction.

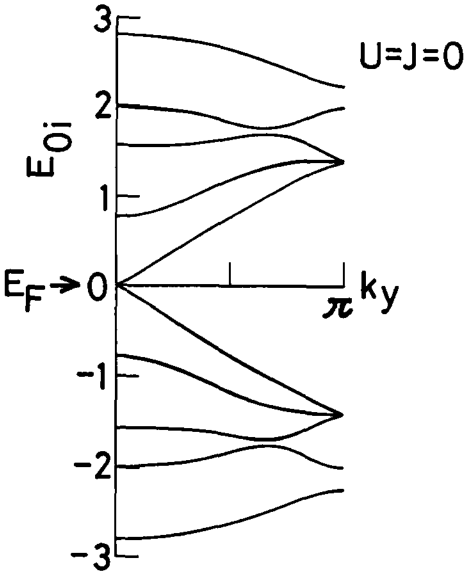

FIGURE 3 Eleven energy bands of π electrons along the direction of k_y axis for $U = J = 0$. E_{0i}, E_F, and k_y denote the energy reduced by t, the Fermi energy, and the wave vector, respectively.

ELECTRONIC AND MAGNETIC PROPERTIES

From Eqs. (9) and (13), the total energy per electron in the magnetic state within the mean-field theory with the periodic boundary condition becomes

$$E_M = 2\sum_{\mathbf{k}}\sum_{i=1}^{6} E_i(\mathbf{k})/11N + \{U\sum_{m=1}^{11}\delta n_m^2 + (13U+J)/4\}/11t, \tag{15}$$

while the energy per electron in the non-magnetic state becomes

$$E_{NM} = 2\sum_{\mathbf{k}}\sum_{i=1}^{6} E_{0i}(\mathbf{k})/11N + U/4t, \tag{16}$$

where $E_{0i}(\mathbf{k})$ is got from Eq. (13) with $\delta n_m = 0$.

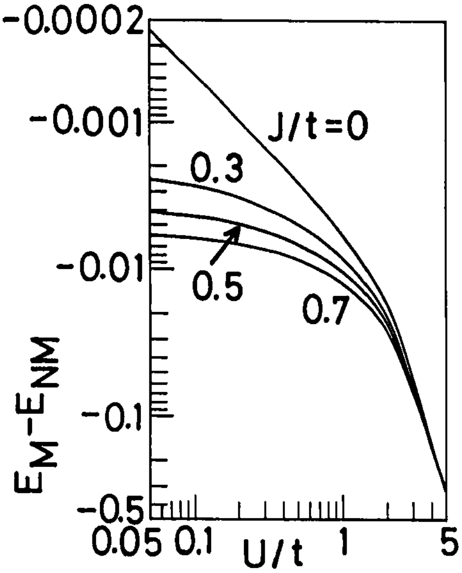

FIGURE 4 Total energy per electron referenced to the nonmagnetic state as a function of U/t for $J/t = 0$, 0.3, 0.5 and 0.7. E_M denotes the total energy per electron in the magnetic state and E_{NM} that in the nonmagnetic one.

Figure 4 shows the total energy per electron referenced to the non-magnetic state as a function of U/t. One sees that the magnetic (spin-density-wave) state is stabilized more by the spin polarization as U/t increases, because the total energy referenced from the nonmagnetic state without spin polarization decreases as U/t increases.

By solving Eqs. (13) and (14) self-consistently, we get the energy bands and

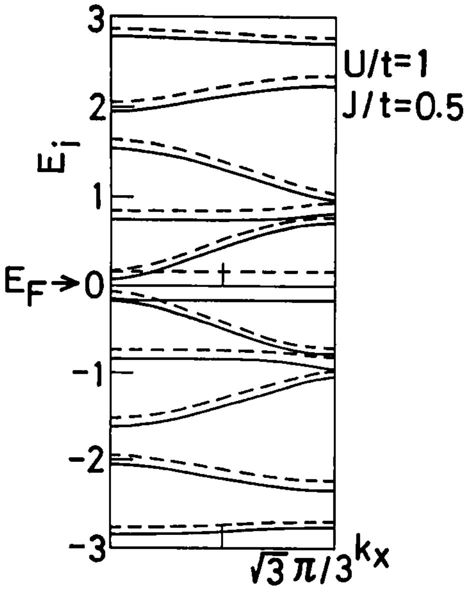

FIGURE 5 Energy bands along the direction of wave vector k_x axis for $U/t = 1$ and $J/t = 0.5$. The solid (dashed) lines are the up (down)-spin bands, and E_i and E_F the energy reduced by t and the Fermi energy, respectively.

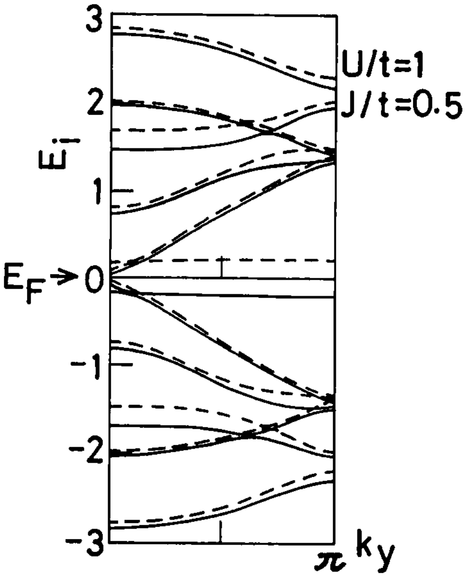

FIGURE 6 Energy bands along the direction of wave vector k_y axis for $U/t = 1$ and $J/t = 0.5$. The solid (dashed) lines are the up (down)-spin bands, and E_i and E_F are the energy reduced by t and the Fermi energy, respectively.

the spin densities. We set $U/t = 1$ and $J/t = 0.5$ in the Q2D hydrocarbon as in the Q1D m-polydiphenylcarbene.[5] Figures 5 and 6 show the energy bands along the directions of k_x and k_y axes, respectively. The solid and dashed lines indicate the up- and down-spin bands, which have the six (five) and five (six) bands having negative (positive) energy, respectively. As the six up- and five down-spin bands have negative energyies, these bands are filled by up- and down-spin electrons in the ground state. The six up-spin bands having negative energies and the six down-spin bands having positive ones are symmetric with respect to the Fermi energy because of the symmetry between up-spin electron and down-spin hole.

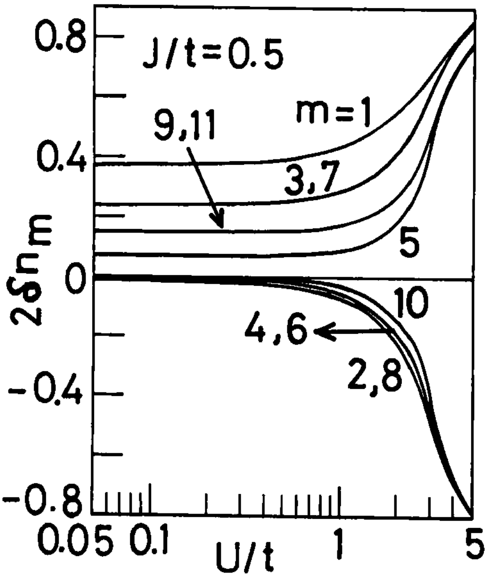

FIGURE 7 The spin density $2\delta n_m$ of π electrons at site m as a function of U/t for $J/t = 0.5$.

Figure 7 depicts the spin density $2\delta n_m$ of π electrons at site m as a function of the on-site Coulomb interaction reduced by the transfer energy, U/t, for $J/t = 0.5$. It is shown that the carbon atoms at odd (even) sites have positive (negative) spin densities and the amplitude of positive spin densities are lager than those of negative ones for $0.05 < U/t < 5$, and all spins at bridging sites become parallel in this π-electron system, namely, this system has a ferromagnetic(ferrimagnetic)-spin-density distribution. The amplitude of the spin density increases abruptly above 1 as U/t

increases, and tends to 1 as U/t goes to infinity.

CONCLUSION AND DISCUSSION

The new Q2D hydrocarbon has been described by the Kondo-Hubbard model with a π electron per carbon atom. The total energy per electron, the energy bands, and the spin densities have been computed within the mean-field theory. It has been found that the ferromagnetic (ferrimagnetic) state is stabilized by the Coulomb-repulsive and ferromagnetic-exchange interactions and all spins at bridging sites become parallel in this π-electron system.

In this study, the Kondo-Hubbard model is defined on the bipartite lattice which has a flat band at the center of the energy spectrum, E_F, as shown in Figures 2 and 3. The six odd-numbered sites have positive spin densities and the five even-numbered sites have negative spin densities due to the antiferromagnetic correlation, as shown in Figure 7. In this model, the itinerant π electron at bridging carbon atom couples the localized spin throuhg the ferromagnetic-exchange coupling J. The electron transfer between the π orbital and the nonbonding one is neglected, because the two orbitals are orthogonal with each other. As shown in Figure 4, as J/t increases from 0 to 0.7, the total magnetic energy per electron referenced to the nonmagnetic state becomes lower for $0.05< U/t <5$. The difference between the magnetic energy for $J = 0$ and that for $J = 0.3, 0.5$, or 0.7 becomes smaller with the increase of U/t from 0.05 to 5. The amplitude of π-electron spin density is most largest at bridging carbon atom among the carbon sites for $J/t = 0.5$, as shown in Figure 7. All spins at bridging sites become parallel in this π-electron system. Thus the Kondo coupling stabilizes ferromagnetism of the π-electron system in the Kondo-Hubbard model.

Lieb[10] proved rigorously that the ground state has spin $S = ||B| - |A||/2$ ($|B|$ ($|A|$) is the number of sites in the B (A) sublattice) in the repulsive Hubbard model with a bipartite lattice and a half-filled band in all dimensions. He suggested an itinerant-electron ferromagnetism in a periodic lattice with $|B| > |A|$. We have pointed out that ferromagnetism appears in the Q2D hydrocarbon with the topological structure, i.e., all spins at bridging carbon atoms becomes parallel in this π-electron system. Within the mean-field approach, the quantum fluctuations are neglected and the critical value for the occurrence of ferromagnetism is the infinitesimal. The interlayer interactions are also important for the appearence of the ferromagnetic long-range order. The effects of quantum fluctuations and interlayer interactions will be studied in future. It is expected that hydrocarbons showing a ferromagnetic long-range order will be synthesized in future.

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