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Critical behaviour of coupled organic ferromagnet chains*

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The interchain coupling in a model, which is most relevant to organic ferromagnets, is studied by a kind of mean field theory. A full phase diagram is given for this model. It is shown that the interchain coupling dramatically affects the ferromagnetic order in the ground state. When the interchain coupling reaches a critical value, the high-spin ground state disappears and the system may transit from ferromagnetic phase into Kondo-singlet phase.

Keywords: interchain coupling, organic ferromagnets, dimerization
PACC: 7550D, 0570F

1. Introduction

Because of the potential technical application, recently the organic ferromagnets have aroused great interest[1−6] since several magnetic organic compounds have been discovered, such as m-PDPC[7] and p-NPNN.[8] This new class of ferromagnetic (FM) material does not have d or f electrons, but can still display the magnetic order. So the mechanism of organic ferromagnets must be quite different from the usual magnetic materials. For experimental work, an important aim is to find a way of synthesizing high-spin ground-state organic polymers. In this direction, Ovchinnikov and Spector[9] attached free radicals to the carbon chain as side groups, as schematically shown in Fig.1. In this structure, the ferromagnetic order was found at room temperature.

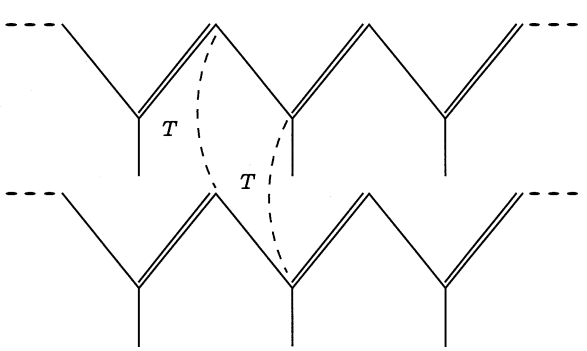


Fig.1. Two neighboring chains of interchain coupled organic ferromagnet.

In theoretical works, there is a basic model to describe this kind of materials. In this model, the π-electrons on the carbon main chain are described by the SSH (Su–Schrieffer–Heeger) model, and the unpaired electron is modelled by a local spin interacting with the π-electron through a Kondo-like interaction. Employing this model, recent theoretical works[10] predicted that the materials always display FM order. In fact, only a few of the materials have been found to show FM order in experimental works. The discrepancy between experiments and theoretical works urges people to exploit the mechanism of FM order. In our previous work,[10] we reconsidered the basic model and found that even in such a simple model there still exists a new mechanism which has not been revealed. After we carefully treated the interaction between local spins and π-electrons, a new phase is found, in which the hybridization effect is included. This effect has always been neglected in previous treatment.

Recent studies[12] show that the interchain coupling between the basic chains is very important and may have a significant effect. For some kinds of interchain coupling structure, the interchain coupling may decrease the energy gap and destabilize the ferromagnetic ground state of the system. However, for the properly selected structure of interchain coupling, it may stabilize high-spin ground state. These results indicate that the interchain coupling plays a very important role in forming FM ground state. So it is

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necessary to study the effects of interchain coupling in more details. For this issue, in previous studies the spin freedom of π-electrons and local spins are completely separated by mean field theory. This kind of treatment just considers the polarization of the conduction electrons by the local spins, while the hybridization between the local spins and the π-electrons is overlooked. The latter part is shown to be important for strong interaction between the local spins and the π-electrons. The hybridization can even destroy the high-spin ground state. In the present work, we reexamine the effect of interchain coupling by a kind of mean field theory, by which one can treat the hybridization and polarization between the local spins and the π-electrons on an equal footing. This is the main motivation of this work.

This paper is arranged as follows: first we give our model Hamiltonian and the treatment of this model. In our results, a full phase diagram is given. Based on this diagram, we then present our discussion and conclusion in the last part.

2. The model Hamiltonian and mean field theory

The model Hamiltonian studied in our paper can be written as

$$H = H_1 + H_2, \tag{1}$$

$$\begin{aligned} H_1 =& -t_0 \sum_{l,i,\sigma} \left[1 + (-1)^i \alpha (u_{l,i} - u_{l,i+1})\right] \\ & \times (c^{\dagger}_{l,i,\sigma} c_{l,i+1,\sigma} + \text{h.c.}) \\ & + J \sum_{R_{l,i}} \mathbf{S}_{R_{l,i}} \cdot \tau_{R_{l,i}} + \frac{K}{2} \sum_{l,i} (u_{l,i} - u_{l,i+1})^2, \end{aligned} \tag{2}$$

$$H_2 = -T \sum_{i,\sigma} (c^{\dagger}_{1,i,\sigma} c_{2,i,\sigma} + \text{h.c.}), \tag{3}$$

in which t_0 is the hopping integral of π-electrons along each main chain when there is no dimerization, α is the electron-lattice coupling constant, $u_{l,i}$ is the lattice distortion of the ith lattice in the lth (l=1,2) main chain. $c^{\dagger}_{l,i,\sigma}(c_{l,i,\sigma})$ denotes the creation (annihilation) operator of π-electron with spin σ at the ith site in the lth chain. The second part of (2) describes the correlation between the radical local spin $S_{R_{l,i}}$ and the π-electron $\tau_{R_{l,i}}$, which can be defined as: $\tau_{R_i} = \sum_{\alpha\beta} c^{\dagger}_{R_{l,i},\alpha} (\boldsymbol{\sigma}_{\alpha\beta}/2) c_{R_{l,i},\beta}$, where $\boldsymbol{\sigma}_{\alpha\beta}$ are the Paul matrices. Strong electron-phonon interaction is considered adiabatically. So the uniform dimerization is assumed in our treatment: $\alpha(u_{l,i} - u_{l,i+1}) = \delta$. The third part of Eq.(2) is the lattice elastic energy, and K is the effective lattice spring constant. In the following treatment, we take t_0 as the unit of energy and use dimensionless electron-lattice coupling: $\lambda = \alpha^2 t_0/K$. H_2 describes the interchain coupling, in which T is the hopping integral from site i of one chain to the corresponding site i of another chain. Here the case of constant interchain coupling strength is considered. In this model we neglect the on-site Coulomb interaction and assume that the interaction just affects the ground state quantitatively. This point can be understood by considering the effects of on-site Coulomb interaction in the Kondo-lattice model (KLM)[13] and SSH model.[14] It should be noted that, if there is no interchain coupling, the model is a special kind KLM and in the usual KLM, there are local impurities on all lattice sites regardless of the electron-lattice coupling.

A similar model has been studied in previous theoretical works.[10,15,16] However, the properties of this model are still far from fully understood. For example, the full phase diagram has still not been given at present. In previous treatments, the transverse interaction between the local spins and the π-electrons is omitted and only the longitudinal interaction is considered. So the transverse interaction effect is totally neglected. In this paper, we treat the longitudinal and transverse interaction on an equal footing and give a full phase diagram for this model on the basis of a mean-field theory[17] which was used to study the coexistence effect in the KLM. We find that the transverse part is very important and also can destroy the ferromagnetic ground state in the coupled chain model.

First we write the local spin in the pseudo-fermion representation:

$$\begin{aligned} S^{+}_{l,i} =& d^{\dagger}_{l,i,\uparrow} d_{l,i,\downarrow}, \\ S^{-}_{l,i} =& d^{\dagger}_{l,i,\downarrow} d_{l,i,\uparrow}, \\ S^{Z}_{l,i} =& (d^{\dagger}_{l,i,\uparrow} d_{l,i,\uparrow} - d^{\dagger}_{l,i,\downarrow} d_{l,i,\downarrow})/2. \end{aligned}$$

Then we divide the π-electrons of each chain into two sublattices, A and B. The site with a radical is expressed using fermion operator b_l, while site without a radical is expressed using a_l. Then the Hamiltonian can be written in the following form:

$$
\begin{aligned}
H = & \sum_{l,i\in A,\sigma} \Big\{(1-\delta)[b^{\dagger}_{l,i+1,\sigma}a_{l,i,\sigma} + \text{h.c.}] + (1+\delta)[b^{\dagger}_{l,i-1,\sigma}a_{l,i,\sigma} + \text{h.c.}]\Big\} \\
& + \frac{J}{4}\sum_{l,i\in A}(b^{\dagger}_{l,i,\uparrow}b_{l,i,\uparrow} - b^{\dagger}_{l,i,\downarrow}b_{l,i,\downarrow})(d^{\dagger}_{l,i,\uparrow}d_{l,i,\uparrow} - d^{\dagger}_{l,i,\downarrow}d_{l,i,\downarrow}) \\
& + \frac{J}{2}\sum_{l,i\in A}(d^{\dagger}_{l,i,\downarrow}d_{l,i,\uparrow}b^{\dagger}_{l,i,\uparrow}b_{l,i,\downarrow} + d^{\dagger}_{l,i,\uparrow}d_{l,i,\downarrow}b^{\dagger}_{l,i,\downarrow}b_{l,i,\uparrow}) + \frac{N\delta^2}{\lambda} \\
& - T\sum_{i\in A,\sigma}\Big[(a^{\dagger}_{1,i,\sigma}a_{2,i,\sigma} + \text{h.c.}) + (b^{\dagger}_{1,i,\sigma}b_{2,i,\sigma} + \text{h.c.})\Big]. \qquad (4)
\end{aligned}
$$

Here we give the longitudinal and transverse interactions separately in Eq.(4) for convenience. The longitudinal interaction term in Eq.(4) is approximated as

$$
\begin{aligned}
J\sum_{l,i\in A} S^Z_{l,i}\tau^Z_{l,i} = & \frac{J}{2}\sum_{l,i\in A}[m_d(b^{\dagger}_{l,i,\uparrow}b_{l,i,\uparrow} - b^{\dagger}_{l,i,\downarrow}b_{l,i,\downarrow}) \\
& + m_b(d^{\dagger}_{l,i,\uparrow}d_{l,i,\uparrow} - d^{\dagger}_{l,i,\uparrow}d_{l,i,\uparrow})] \\
& + \frac{Jm_bm_dN}{2}, \qquad (5)
\end{aligned}
$$

where we have introduced the order parameter m_d to characterize the ferromagnetic order of the local spin:

$$
m_d = \frac{\left\langle d^{\dagger}_{l,i,\uparrow}d_{l,i,\uparrow} - d^{\dagger}_{l,i,\downarrow}d_{l,i,\downarrow}\right\rangle}{2}. \qquad (6)
$$

Also, the magnetic order of π-electron in main chain is described by the following two order parameters:

$$
m_b = \frac{\left\langle b^{\dagger}_{l,i,\uparrow}b_{l,i,\uparrow} - b^{\dagger}_{l,i,\downarrow}b_{l,i,\downarrow}\right\rangle}{2}, \qquad (7)
$$

$$
m_a = \frac{\left\langle a^{\dagger}_{l,i,\uparrow}a_{l,i,\uparrow} - a^{\dagger}_{l,i,\downarrow}a_{l,i,\downarrow}\right\rangle}{2}. \qquad (8)
$$

These two parameters are the expectation values of τ^Z_i at odd sites and even sites, respectively. According to the mean-field form of the longitudinal interaction, one can clearly find that the effect of this term is just like that of magnetic field applied on the sites with radicals. So this term describes the effect of polarization of the π-electrons caused by the free radicals.

The transverse interaction term is approximated as

$$
\begin{aligned}
& \frac{J}{2}\sum_{l,i\in A}(S^+_{l,i}\tau^-_{l,i} + \text{h.c.}) \\
= & \frac{JV}{2}\sum_{l,i\in A,\sigma}(b^{\dagger}_{l,i,\sigma}d_{l,i,\sigma} + d^{\dagger}_{l,i,\sigma}b_{l,i,\sigma}) + \frac{J}{2}V^2N,
\end{aligned}
$$

where the order parameter V describes the hybridization between the local spin and π-electron and

$$
\begin{aligned}
V = & -\left\langle b^{\dagger}_{l,i,\uparrow}d_{l,i,\uparrow} + d^{\dagger}_{l,i,\downarrow}b_{l,i,\downarrow}\right\rangle \\
= & -\left\langle b^{\dagger}_{l,i,\downarrow}d_{l,i,\downarrow} + d^{\dagger}_{l,i,\uparrow}b_{l,i,\uparrow}\right\rangle, \qquad (9)
\end{aligned}
$$

which reflects the local Kondo-singlet state.[8] By this treatment, we can exactly diagonalize the remainder of the Hamiltonian. It should be noted that, since the two chains in this system are identical, the order parameters above are equal in each chain. Therefore, we can rewrite the Hamiltonian (4) in momentum space:

$$
\begin{aligned}
H = & \sum_{k,\sigma}\Gamma^{\dagger}_{k,\sigma}\hat{H}_{k,\sigma}\Gamma_{k,\sigma} + \frac{J}{2}NV^2 \\
& - Jm_bm_dN + \frac{N\delta^2}{\lambda}, \qquad (10)
\end{aligned}
$$

where $\Gamma^{\dagger}_{k,\sigma} = (b^{\dagger}_{1,k,\sigma}, a^{\dagger}_{1,k,\sigma}, d^{\dagger}_{1,k,\sigma}, b^{\dagger}_{2,k,\sigma}, a^{\dagger}_{2,k,\sigma}, d^{\dagger}_{2,k,\sigma})$, and

$$
\hat{H}_{k,\sigma} = \begin{pmatrix}
\frac{Jm_d\sigma}{2} & f & \frac{JV}{2} & T & 0 & 0 \\
f^* & 0 & 0 & 0 & T & 0 \\
\frac{JV}{2} & 0 & \frac{Jm_b\sigma}{2} & 0 & 0 & 0 \\
T & 0 & 0 & \frac{Jm_d\sigma}{2} & f & \frac{JV}{2} \\
0 & T & 0 & f^* & 0 & 0 \\
0 & 0 & 0 & \frac{JV}{2} & 0 & \frac{Jm_b\sigma}{2}
\end{pmatrix}.
$$

In the above matrix, $f = 2\left[\cos(k) + \mathrm{i}\delta\sin(k)\right]$. The Brillouin zone is folded in half, so the summation over k is carried out in the reduced Brillouin zone: $|k| \leq \pi/2$. The quasiparticle spectra are determined by the equation: $\left|\hat{H} - E\hat{I}\right| = 0$, then twelve energy bands will emerge. As we completely fill the six lowest energy bands, the ground state energy can be written as

$$E_{\mathrm{GS}} = \sum_{k,i=1,\ldots,6} E_i(k) + \frac{J}{2}NV^2 - Jm_b m_d N + \frac{N\delta^2}{\lambda},$$

where $E_i(k)$ $(i = 1,\ldots,6)$ are the lowest six energy bands. The self-consistent equations for the three relevant order parameters (m_d,, m_b, and V) can be obtained by calculating the expectation values in equations (6, 7, 9). In fact there is the fourth order parameter: the lattice dimerization δ, which can be obtained by minimizing the ground state energy: $\partial E_{\mathrm{GS}}/\partial\delta = 0$, $\partial^2 E_{\mathrm{GS}}/\partial\delta^2 > 0$. All of these order parameters can be calculated numerically.

3. Results

In the following calculation, we take the parameters $\lambda = 0.5$. The order parameters are calculated with increasing the interchain coupling. For $J = 2$, the calculation results are shown in Fig.2. One may find that, as T is small, the order parameter m_d is exactly equal to $1/2$, which means that the local radical spins are ferromagnetically arranged. And the electrons in the main chain are distributed antiferromagnetically. This point can be seen from the value of m_a and m_b, which have the same absolute value with opposite signs. And the Kondo-singlet order parameter V is zero. We call this phase dimerized ferromagnetic (DFM) phase. When T is increased to a critical value T_1^c, the parameter m_d falls abruptly to a value smaller than $1/2$; and the dimerization parameter δ is zero. V jumps from zero to a finite value. That is to say, in such a situation, the dimerization is totally destroyed and the hybridization between the local spin and π-electron is enhanced. In this phase, the values of the order parameter m_d and V both are finite. It seems that there is a coexisting (CO) phase of FM and Kondo singlet state. With increasing the interchain coupling, one may find that m_d, $|m_a|$ and $|m_b|$ are all decreased. These phenomena imply that the magnetic orders in main chain and radicals are all suppressed by the interchain coupling. At the same time, the order parameter V increased monotonically and the hybridization effect is enhanced.

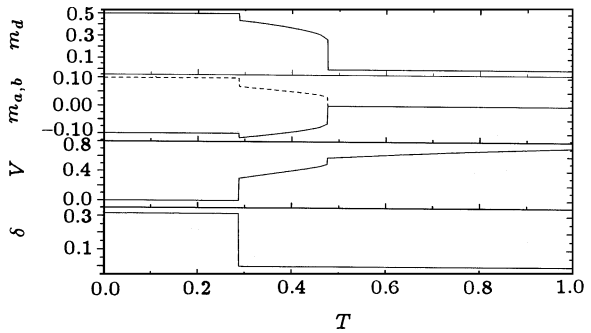


Fig.2. The order parameter versus interchain coupling T, λ=0.5, $J = 2$, the dotted line is m_a.

As T reaches to a critical value T_2^c, m_d, $|m_a|$ and $|m_b|$ all have zero value, and V has a finite value. The magnetic order in the main chain and radicals entirely disappear. Since the finite order parameter is V, in this phase the ordered phase is Kondo singlet (KS) phase.

Above results suggest that, even in such a simple model, there still exist rich phases. Summing up the above results, a full phase diagram is given in Fig.3. In this figure, the dotted line represents the transition from DFM phase to the CO phase, and the transition from CO phase to KS phase is represented by solid line. It should be noted that these two phase transitions are both first order in our theoretical frame.

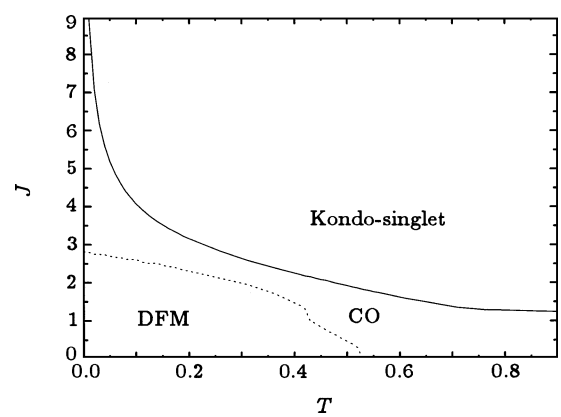


Fig.3. Full phase diagram of our model. The dotted line represents the transition from the DFM phase to the CO and the solid line represents the transition from the CO phase to the Kondo-singlet phase.

4. Discussion and conclusions

Now we give a brief discussion on the above results. By the phase diagram, one may find that with increasing the interchain coupling or Kondo-like coupling, the system can be driven to the KS phase. But

this is by no means to imply that their effects are the same. One should keep in mind that without the Kondo-like coupling, there is no FM state. There are two parts in Kondo-like coupling. The longitudinal part gives polarization effect, which is the main contributor to the FM state. However, the transverse part results in a hybridization effect, which favours the random Kondo-singlet state. The situation for interchain coupling is quite different, although they all seem to be against the FM state. The interchain coupling does not directly affect the magnetic order. This point can be seen from the phase diagram, in which one can find that, as $J \lesssim 1$, with increasing the interchain coupling T, the system cannot be driven to the KS phase. That is to say, the interchain coupling has little contribution to the hybridization between the local spins and π-electrons, but it can reduce the polarization effects in Kondo-like interaction J. This point is also confirmed in Yao's works,[12] in which only the polarization effect is considered and the interchain coupling can completely destroy the FM phase. As $J \lesssim 1$, by reducing the polarization effects, the interchain coupling can drive the system to the KS state.

In physics, the effect of interchain coupling can be simply understood as this: since the π-electrons spend time hopping from one chain to another, the chance of being polarized by local spin is lowered. Then the effect of polarization will be suppressed. At the same time, the interchain hopping is helpful to uniform distribution of π-electrons in main chains. So this coupling will suppress the dimerization, which is helpful to stabilize the FM state. These two mechanisms will destabilize the FM ground state colour. One may also think that interchain coupling can reduce the hybridization effect under our physical picture. But we argue that the interchain coupling have more effect on polarization than on hybridization. For this argument, the anisotropy effects of the Kondo-like interaction between the local spin and π-electron should be considered. Such kind of results will be given in our future work.

For material synthesis, the materials should have small T and J. If J is small enough, the effect of interchain coupling need not to be considered, since it just can drive the materials to the CO phase, in which the FM state is partly retained. So, in this situation, the interchain coupling strength has little effect on the FM state. The materials which have smaller J will be more suitable for synthesizing high-spin ferromagnets.

In conclusion, we have investigated a quasi-one-dimensional organic polymer ferromagnet model with interchain coupling. With increasing interchain coupling, one can find that the system may transit from DFM phase to KS phase. Between these two phases, there is a phase in which the FM phase and KS phase can coexist. Based on the full phase diagram, we argue that for small enough J, the effect of interchain coupling can be neglected. But when J is large, the interchain coupling should be considered. It has dramatic effects on the ground state properties.

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