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Critical behaviour of organic ferromagnets

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Abstract

The phase diagram of the quasi-one-dimensional model which is most relevant to organic ferromagnets of a certain kind is considered. In this model, strong electron–phonon interaction is considered adiabatically and the coupling between local spins and π-electrons is treated within a mean-field theory. A full phase diagram is given. The results show that there are two new kinds of phase which were not revealed in previous treatments. Our results may be helpful for the synthesis of organic ferromagnets.

1. Introduction

Since the discovery of the organic ferromagnets (OFs)—such as m-PDPC [1] and p-NPNN [2]—great attention has been paid to these materials. The most interesting thing about the OF is that there are no magnetic ions, but it can display ferromagnetism. In experimental work, one important aim has been to find a method of synthesis of high-spin ground-state organic polymers. In this direction, Ovchinnikov and Spector [3] attached free radicals to the carbon chain as side groups; there is one unpaired electron on each free radical. In this structure, which is a quasi-1D material, ferromagnetic order was found at room temperature. However, up to now, only a few of the materials have been found to show ferromagnetic order.

In theoretical work, much effort [4, 5] has been concentrated on this issue. Several models [6] have been proposed for studying the ferromagnetic properties of these materials. The main feature of the model generally used is that the π-electrons on the carbon main chain are described by the SSH (Su–Schrieffer–Heeger) model plus on-site Coulomb interaction, and the unpaired electron is modelled by a local spin, which interacts with the π-electrons through a Kondo-like interaction. Recent studies [6] show that this kind of system is always a stable ferromagnetic state. That is to say, *any material with such structure must have ferromagnetic order*. However, as we mentioned above, only a small proportion of the materials with this structure do actually show ferromagnetic properties. Naturally, questions arise: what is the reason for the discrepancy between the theory and experiment, and how does one explain the non-ferromagnetic state, which cannot be obtained from the model usually used. It can be concluded that there must exist mechanisms which disfavour the high-spin ferromagnetic

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ground state. Studying these mechanisms is necessary and helpful for material synthesis. It will suggest ways of finding OF materials.

In materials with this kind of structure, the properties of the system arise from the interplay between dimerization and Kondo-like interaction. The former will result in a singlet ground state for the conduction electrons. The latter will have more complicated effects. Findings derived from the Kondo-lattice model (KLM) [7] indicate that this interaction will have two effects. We divide the interaction into longitudinal and transverse parts. The former is a polarization effect caused by the local spins; it will result in an antiferromagnetic long-range order, and this order and the dimerization will mutually conflict. The latter will yield a disordered Kondo-singlet state for conduction electrons. It is obvious that this effect will destroy the conduction electron singlet; that is to say, the dimerization will be unstable when this effect appears. It is interesting that all of these interactions are displayed in one system. As regards the potential for technical application, studying the magnetic order is the most important area. So we will pay most attention to the influence of interactions on the magnetic order of the system. In this work, all of the above mechanisms can be seen by appropriately varying the order parameter.

2. The model Hamiltonian and mean-field theory

The model Hamiltonian relevant to the OFs can be written as [6]

$$H = -t \sum_{i,\sigma} \left[1 + (-1)^i \alpha(u_i - u_{i+1})\right] (c^\dagger_{i,\sigma} c_{i+1,\sigma} + \text{h.c.}) + J \sum_{R_i} \boldsymbol{S}_{R_i} \cdot \boldsymbol{\tau}_{R_i} + \frac{K}{2} \sum_i (u_i - u_{i+1})^2 \qquad (1)$$

in which $\boldsymbol{S}_{R_i}$ is the radical local spin and $\boldsymbol{\tau}_{R_i}$ is the spin of the electrons in the conduction band, which can be defined as

$$\boldsymbol{\tau}_{R_i} = \sum_{\alpha\beta} c^\dagger_{R_i,\alpha} (\vec{\sigma}_{\alpha\beta}/2) c_{R_i,\beta}$$

where the $\vec{\sigma}_{\alpha\beta}$ are the Paul matrices. Here strong electron–phonon interaction is considered adiabatically. α is the electron–lattice coupling constant. u_i is the lattice distortion of the ith lattice. Also, uniform dimerization is assumed in this work: $\alpha(u_i - u_{i+1}) = \delta$. Here, we study the simplest case: there is only one carbon between two neighbouring side radicals. Then the second term of (1) can be simply written as

$$J \sum_{i\ \text{odd}} \boldsymbol{S}_i \cdot \boldsymbol{\tau}_i \qquad \text{or} \qquad J \sum_{i\ \text{even}} \boldsymbol{S}_i \cdot \boldsymbol{\tau}_i.$$

Also, the last term of the model Hamiltonian is the lattice elastic energy; K is the effective lattice spring constant. In the following we take t as the unit of energy and use dimensionless electron–lattice coupling: $\lambda = \alpha^2 t/K$. In this model, the on-site Coulomb interaction is not included. We believe that this interaction just affects the ground state quantitatively. This point can be understood by considering the effects of on-site Coulomb interaction in the KLM [8] and the SSH model [9]. It should be noted that this model is also interesting in the context of the KLM, which is the model most relevant to heavy-fermion compounds. It is a special kind of KLM; in the usual KLM, there are local impurities on all lattice sites regardless of the electron–lattice coupling.

A similar model has been extensively studied in previous theoretical work. However, the properties of this model are still far from being fully understood; for example, up to now the full phase diagram has still not been given. In previous studies, the transverse interaction between the local spin and the π-electrons was omitted and only the longitudinal interaction was considered [6]. Obviously, in such a treatment the effect of transverse interaction is totally disregarded. It is the main purpose of this paper to reconsider this problem. We will treat the longitudinal and transverse interactions on an equal footing and give a full phase diagram for this model on the basis of a mean-field theory [10] which is used to study the coexistence effect in the KLM. We find that the transverse part is very important and can destroy the ferromagnetic ground state.

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

$$S_i^z = (d_{i\uparrow}^\dagger d_{i\downarrow} - d_{i\uparrow}^\dagger d_{i\downarrow})/2 \qquad S_i^- = d_{i\downarrow}^\dagger d_{i\uparrow} \qquad S_i^+ = d_{i\uparrow}^\dagger d_{i\downarrow}.$$

Then we divide the π-electrons into two sublattices, A and B, according to the site number. The site with a radical is expressed using fermion operator b, while that without a radical is expressed using a. Then the Hamiltonian can be written in terms of b and a:

$$\begin{aligned} H = \sum_{i\in \mathrm{A},\sigma} & \left\{(1-\delta)[b_{i+1,\sigma}^\dagger a_{i,\sigma} + \mathrm{h.c.}] + (1+\delta)[b_{i-1,\sigma}^\dagger a_{i,\sigma} + \mathrm{h.c.}]\right\} + \frac{N\delta^2}{2\lambda} \\ & + \frac{J}{4}\sum_{i\in \mathrm{A}}(b_{i\uparrow}^\dagger b_{i\uparrow} - b_{i\downarrow}^\dagger b_{i\downarrow})(d_{i\uparrow}^\dagger d_{i\uparrow} - d_{i\downarrow}^\dagger d_{i\downarrow}) \\ & + \frac{J}{2}\sum_{i\in \mathrm{A}}(d_{i\downarrow}^\dagger d_{i\uparrow} b_{i\uparrow}^\dagger b_{i\downarrow} + d_{i\uparrow}^\dagger d_{i\downarrow} b_{i\downarrow}^\dagger b_{i\uparrow}). \end{aligned} \tag{2}$$

In the last two terms of equation (2), for convenience we give the longitudinal and transverse interactions separately.

In the following we will study ground-state properties on the basis of the above Hamiltonian. The longitudinal interaction term in equation (2) is approximated as

$$J\sum_{i\in \mathrm{A}} S_i^z \tau_i^z = \frac{J}{2}\left[m_d \sum_{i\in \mathrm{A}}(b_{i\uparrow}^\dagger b_{i\downarrow} - b_{i\uparrow}^\dagger b_{i\downarrow}) + m_b(d_{i\uparrow}^\dagger d_{i\downarrow} - d_{i\uparrow}^\dagger d_{i\downarrow})\right] + \frac{J m_b m_d N}{2} \tag{3}$$

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

$$m_d = \frac{\left\langle d_{i\uparrow}^\dagger d_{i\uparrow} - d_{i\downarrow}^\dagger d_{i\downarrow}\right\rangle}{2}. \tag{4}$$

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

$$m_b = \frac{\left\langle b_{i\uparrow}^\dagger b_{i\uparrow} - b_{i\downarrow}^\dagger b_{i\downarrow}\right\rangle}{2} \tag{5}$$

$$m_a = \frac{\left\langle a_{i\uparrow}^\dagger a_{i\uparrow} - a_{i\downarrow}^\dagger a_{i\downarrow}\right\rangle}{2} \tag{6}$$

which are the expected values of τ_i^z at odd sites and even sites, respectively. From the mean-field form of the longitudinal interaction, one can clearly find that the effect of this term is just like that of a magnetic field applied to 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

$$\frac{J}{2}\sum_{i\in \mathrm{A}}(S_i^+\tau_i^- + \mathrm{h.c.}) = \frac{JV}{2}\sum_{i\in \mathrm{A},\sigma}(c_{i,\sigma}^\dagger d_{i,\sigma} + d_{i,\sigma}^\dagger c_{i,\sigma}) + \frac{J}{4}V^2 N$$

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

$$V = -\left\langle c_{i\uparrow}^{\dagger} d_{i\uparrow} + d_{i\downarrow}^{\dagger} c_{i\downarrow} \right\rangle = -\left\langle c_{i\downarrow}^{\dagger} d_{i\downarrow} + d_{i\uparrow}^{\dagger} c_{i\uparrow} \right\rangle \tag{7}$$

which reflects the local Kondo-singlet state [7]. These treatments allow us to exactly diagonalize the remainder of the Hamiltonian. Then we can rewrite Hamiltonian (2) in momentum space:

$$H = \sum_{k,\sigma} \Gamma_{k,\sigma}^{\dagger} \hat{H}_{k,\sigma} \Gamma_{k,\sigma} + \frac{J}{4} N V^2 - \frac{J m_b m_d N}{2} + \frac{N\delta^2}{2\lambda} \tag{8}$$

where $\Gamma_{k,\sigma}^{\dagger} = (b_{k,\sigma}^{\dagger}, a_{k,\sigma}^{\dagger}, d_{k,\sigma}^{\dagger})$, and the matrix $\hat{H}_{k,\sigma}$ can be expressed as

$$\hat{H}_{k,\sigma} = \begin{pmatrix} \frac{J m_d}{2} & f & \frac{JV}{2} \\ f^{*} & 0 & 0 \\ \frac{JV}{2} & 0 & \frac{J m_b}{2} \end{pmatrix}$$

where $f = 2[\cos(k) + \mathrm{i}\delta \sin(k)]$. Also, the Brillouin zone is folded in half, so the summation over k is carried out in the reduced Brillouin zone: $|k| \leqslant \pi/2$. The quasiparticle spectra are determined by the equation $|\hat{H} - E\hat{I}| = 0$, from which six bands will emerge. The exact forms are very lengthy, so we do not write them out here. As we completely fill the three lowest energy bands, the ground-state energy can be written as

$$E_{GS} = \sum_{k,i=1,2,3} E_i(k) + \frac{J}{4} N V^2 - \frac{J m_b m_d N}{2} + \frac{N\delta^2}{2\lambda}$$

where $E_i(k)$ $(i = 1, 2, 3)$ are the lowest three negative-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 (4), (5), (7). In fact, there is a fourth order parameter: the lattice dimerization δ, which can be obtained by minimizing the ground-state energy: $\partial E_{GS}/\partial\delta = 0$, $\partial^2 E_{GS}/\partial\delta^2 > 0$. All of these order parameters can be calculated numerically.

3. Results

Skipping details, we give the results in figures 1 and 2. In these two figures, for the parameters m_a and m_b, the dotted lines represent m_a, while the solid lines represent m_b. Here we show two typical situations.

In figure 1, for $\lambda = 1$, there is only one phase transition point. In this case, as J is increased from zero, there is a critical point J_c at which the absolute values of the order parameters m_d, m_b decrease discontinuously to a very small value, the dimerization parameter falls to zero, and V jumps from zero to a finite value. When $J < J_c$, m_d is exactly equal to 1/2, which means that the ground states of the local radical spins are ferromagnetically arranged; and the electrons in the main chain are distributed antiferromagnetically. This point can be inferred from the values of m_a and m_b, which have the same absolute value and opposite sign. Also, the Kondo-singlet order parameter V is zero. We call this phase the dimerized ferromagnetic (DFM) phase. When $J > J_c$, the situation is quite different: the values of m_d and m_b fall to a very small value, δ is equal to zero, and V jumps to a large finite value. In this phase, the AF in the main chain and the FM order of the radicals are strongly suppressed; the dimerization is completely destroyed. Also, the Kondo-singlet state is enhanced. This phase can be called a

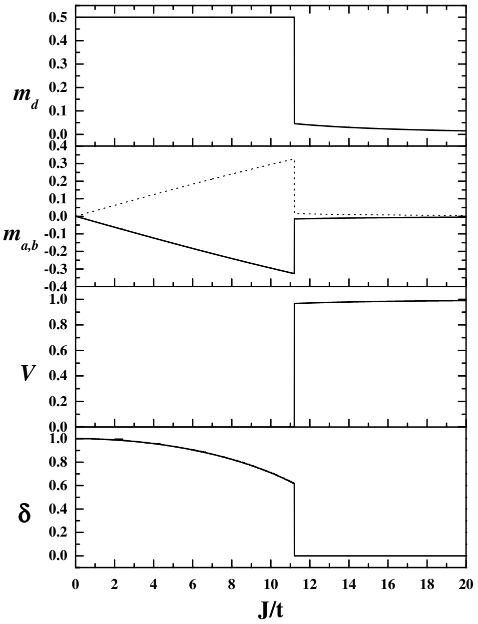

Figure 1. The order parameters versus J/t. The dotted line is for the order parameter m_a. In this figure, $\lambda = 1.0$.

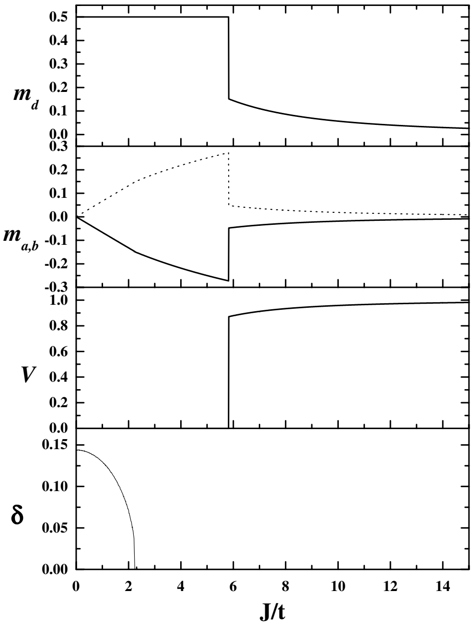

Figure 2. The order parameters versus J/t. The dotted line is for the order parameter m_a. In this figure, $\lambda = 1/3$.

Kondo-singlet-like (KSL) phase. It is not a true Kondo-singlet state, because there is still very weak AF order ($m_a = -m_b \neq 0$) on the main chain.

In figure 2, another typical case is shown. In this figure, the electron–lattice coupling is reduced to $\lambda = 1/3$. Between the DFM and KSL phases, there emerges a new phase. In this phase, the dimerization is fully suppressed, but the FM order is still retained: $m_d = 1/2$, $V = 0$, and $\delta = 0$. So it is a pure FM phase without dimerization and without a Kondo singlet.

Combining the above results, a full phase diagram is given in figure 3. In this figure, the dotted line represents the second-order phase transition from the DFM phase to the FM phase. The transition from the FM phase to the KSL phase is a first-order transition; it is represented by the solid line. In this figure, we apply the restriction $\lambda < 1$, because for common polyacetylene, $\lambda \sim 0.2$ [11]. From this phase diagram, we find that the DFM region will be enlarged as the electron–lattice interaction is increased. When J is strong enough, the high-spin ground-state DFM and FM phases can be replaced by a KSL phase. It should be noted that in the DFM phase there is an energy gap in the quasiparticle excitation, while it is gapless in the FM phase, where there is zero dimerization.

4. Discussion and conclusions

Now we would like to give some space to discussing the above results. As the Kondo-like interaction J is small, the AF phase is determined by the polarization effect, which is given by the longitudinal part. When J is strong enough, the effect of the transverse part will become apparent. Also, the AF phase will be replaced by the random Kondo-singlet state. In our model, there is a vacancy between two nearest free radicals; so the AF phase of the local spin will be changed to a FM one when J is small. It is just as if all up or down spins have been removed from the Néel state, the remaining spins favouring a ferromagnetically ordered

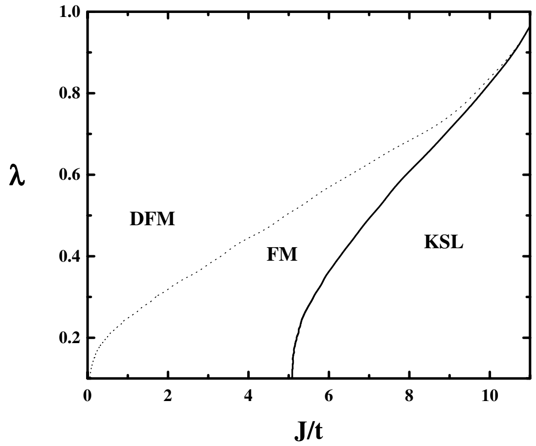

Figure 3. The full phase diagram of our model. The dotted line represents a second-order transition from the DFM phase to the FM phase, while the solid line represents a first-order transition from the FM phase to the KSL phase.

state, which could be inferred from the value of the order parameter: $m_d = 1/2$ for small J. Also, in this effect it is as if there is an effective uniform external field applied to the main dimerized chain. Therefore, as the Kondo-like interaction is increased from zero, the dimerization parameter δ will be monotonically decreased. When J is strong enough, the effects of the transverse part will become apparent and dominate. The π-electron will form a Kondo singlet with a free-radical spin. This singlet will compete with the π-electron singlet in the main chain. When the strength of the electron–lattice coupling is weak enough, only the longitudinal part can fully suppress the dimerization before the transverse part has an effect on the ground state. So two different phase transitions may be seen in this system.

From the phase diagram, we find that for material synthesis, researchers should try to reduce the strength of J in order to get OFs, and strong electron–lattice interaction is favourable to a FM state. That is to say, when we select the main chain for synthesizing OFs, we should consider the strength of the electron–lattice interaction and the properties of the attached free radical. Previous theoretical work has mainly concentrated on the region of the DFM phase. In this work, we find a new FM phase which has no lattice dimerization. The two kinds of ferromagnetic order are different. The energy gap in the DFM phase causes DFM material to be more stable than material in the FM phase, because the dimerization can suppress thermal fluctuation. Also, material in the DFM phase is harder to polarize than material in the FM phase. For applications in magnetic memory, DFM material may be desirable.

In conclusion, using a kind of mean-field theory, we have investigated the ground-state properties of the theoretical model which is most relevant to a kind of quasi-1D organic polymer ferromagnet. A full phase diagram is given in this work. Also, two new phases are found in this model. Our results clearly show that strong electron–lattice interaction can stabilize the FM state, and for strong interaction between the π-electron and the radical, the high-spin FM ground state will be unstable.

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References

[1] Iwamura H, Sugawara T, Itoh K and Takui T 1985 *Mol. Cryst. Liq. Cryst.* **125** 379
[2] Takahashi M, Turek P, Nakazawa Y and Tamura M 1991 *Phys. Rev. Lett.* **67** 746
[3] Ovchinnikov A A and Spector V N 1988 *Synth. Met.* **27** B 615
[4] Nasu K 1986 *Phys. Rev.* B **33** 330
[5] Macêdo A M S, Dos Santos M C, Coutinho-Filho M D and Macêdo C A 1995 *Phys. Rev. Lett.* **74** 1851
[6] Fang Z, Liu Z L and Yao K L 1994 *Phys. Rev.* B **49** 3916
[7] Tsunetsugu H, Sigrist M and Ueda K 1997 *Rev. Mod. Phys.* **69** 809
[8] Chen Y G, Chen H, Yuan Q S and Zhang Y M 1999 *J. Phys.: Condens. Matter* **11** 5623
[9] Otsuka H 1997 *Phys. Rev.* B **56** 15 609
[10] Zhang Guang-Ming and Yu Lu 2000 *Preprint* cond-mat/0004405
[11] Heeger A J, Kivelson S, Schrieffer J R and Su W P 1988 *Rev. Mod. Phys.* **60** 781 and references therein