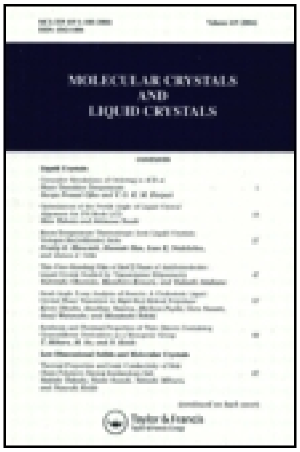

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Magnetic Properties of Organic Af-F Alternating Chains

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MAGNETIC PROPERTIES OF ORGANIC AF-F ALTERNATING CHAINS

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Abstract Magnetic susceptibility and magnetic excitation of antiferromagnetic and ferromagnetic (AF-F) alternating chains are studied by the pair dynamical correlated-effective-field approximation. The static magnetic susceptibility $\chi(T)$ vanishes at $T = 0$ K reflecting the existence of a gap between the singlet ground state and the excited states. At finite temperatures $\chi(T)$ shows a broad maximum around the temperature corresponding to the exchange coupling. The calculated $\chi(T)$ agrees fairly well with the results of exact diagonalization method for finite spins. The magnetic excitation exhibits a minimum value at $q = \pm\pi/2$. This makes a striking contrast with the AF alternating chains in which the magnetic excitation has a minimum at $q = 0$ and $q = \pi$. The magnetic susceptibility of real S=1/2 organic AF-F chains, Cu(TIM)$CuCl_4$ and [Cu(bpym)$(OH)_2$]$\cdot 2H_2O$, are analyzed by our method and inelastic neutron scattering spectra for these systems are calculated.

INTRODUCTION

The one-dimensional magnetic systems have been studied extensively both experimentally and theoretically by chemists and physicists. Examples are spin Peierls systems, Haldane systems and so on. Quite recently other interesting one-dimensional systems, organic antiferromagnetic-ferromagnetic (AF-F) alternating chains have been synthesized, but there are few theoretical works on their magnetic properties[1].

In this paper we apply the pair dynamical correlated effective field approximation (Pair-DCEFA)[2] to calculate the static magnetic susceptibility $\chi(T)$ and the magnetic excitation $\omega(q)$ of AF-F alternating chains. In the Pair-DCEFA the antiferromagnetic spin-pair is solved exactly and the ferromagnetic interaction between the pairs is treated by the DCEFA.[3] The advantage of the Pair-DCEFA are as follows. First, when applied to one-dimensional systems, it gives no finite transition temperature. Secondly, it can be applied to two or three dimensional systems and complicated magnetic systems without difficulty. To confirm the validity and the usefulness of the Pair-DCEFA we compare $\chi(T)$ obtained by the Pair-DCEFA with that obtained by the exact diagonalization method (EDM) for finite spins. Finally we analyse the observed susceptibility of S=1/2 organic AF-F alternating chains

Cu(TIM)CuCl$_4$ and [Cu(bpym)(OH)$_2$]·2H$_2$O and calculate inelastic neutron scattering spectra for these systems.

PAIR-DCEFA

We express the Hamiltonian of the AF-F alternating chain as follows:

$$\mathcal{H} = -\sum_i (J_1\vec{S}_{i,1}\cdot\vec{S}_{i,2} + J_2\vec{S}_{i-1,2}\cdot\vec{S}_{i,1}) \tag{1}$$

where $S_{i,1}(S_{i,2})$ denotes the spin 1 (spin 2) in the unit cell i, and $J_1(<0)$ and $J_2(>0)$ are the antiferromagnetic and ferromagnetic exchange integral, respectively. In the Pair-DCEFA[2] the spin-pair interacting through J_1 is solved exactly and the exchange interaction (J_2) between the pairs is treated by the DCEFA,[3] *i.e.* the following decoupling is adopted

$$\begin{aligned} J_2\vec{S}_{i-1,2}\cdot\vec{S}_{i,1} \;\rightarrow\; & J_2\{\vec{S}_{i,1}\cdot(<\vec{S}_{i-1,2}> -\alpha <\vec{S}_{i,1}>) \\ & +\vec{S}_{i-1,2}\cdot(<\vec{S}_{i,1}> -\alpha <\vec{S}_{i-1,2}>)\}\,, \end{aligned} \tag{2}$$

where $<\vec{S}>$ denotes the spontaneous or the field-induced spin moment and α represents the correlation parameter. If we consider the paramagnetic state, we have $<\vec{S}_{i,1}>=<\vec{S}_{i,2}>=0$, and then the effective pair-spin Hamiltonian for the unit cell i in the Pair-DCEFA can be given simply by

$$\mathcal{H}_i^{\text{eff}} = -J_1\vec{S}_{i,1}\cdot\vec{S}_{i,2}. \tag{3}$$

Now we calculate the transverse susceptibility tensor $\tilde{\chi}^{+-}(q,\omega)$ of the paramagnetic state in the spirit of Pair-DCEFA. For this purpose we apply fictitious rotating magnetic fields for the respective sublattice as follows:

$$\text{sublattice 1}: \quad h^+_{q,1}e^{i(qR_{i,1}-\omega t)}, \tag{4}$$

$$\text{sublattice 2}: \quad h^+_{q,2}e^{i(qR_{i,2}-\omega t)}. \tag{5}$$

By taking into account the field-induced spin moments of the other unit cells in the DCEFA, the effective Zeeman interaction for the i-th unit cell is expressed as

$$\mathcal{H}^{\text{eff}}_{i,\text{Zeeman}} = -F_1S^-_{i,1} - F_2S^-_{i,2}, \tag{6}$$

where

$$F_1 = h^+_{q,1}e^{i(qR_{i,1}-\omega t)} + \frac{J_2}{2}(<S^+_{i-1,2}> -\alpha <S^+_{i,1}>), \tag{7}$$

$$F_2 = h^+_{q,2}e^{i(qR_{i,2}-\omega t)} + \frac{J_2}{2}(<S^+_{i+1,1}> -\alpha <S^+_{i,2}>). \tag{8}$$

Now, within the linear response approximation we get the following relations:

$$< S_{i,1}^{+} > = \phi_{11}^{+-}(\omega)F_1 + \phi_{12}^{+-}(\omega)F_2, \tag{9}$$

$$< S_{i,2}^{+} > = \phi_{21}^{+-}(\omega)F_1 + \phi_{22}^{+-}(\omega)F_2. \tag{10}$$

Here $\phi_{ij}^{+-}(\omega)$ $(i, j{=}1,\ 2)$ denotes the pair-spin susceptibility calculated on the basis of the effective pair-spin Hamiltonian eq.(3) and in the case of $S_1{=}S_2{=}1/2$ its expression is given explicitly as follows:

$$\phi_{11}^{+-} = \phi_{22}^{+-} = \beta\rho_1\delta_{\omega,0} + \frac{1}{2}(\rho_1 - \rho_2)(\frac{1}{\omega + J_1} - \frac{1}{\omega - J_1}), \tag{11}$$

$$\phi_{12}^{+-} = \phi_{21}^{+-} = \beta\rho_1\delta_{\omega,0} - \frac{1}{2}(\rho_1 - \rho_2)(\frac{1}{\omega + J_1} - \frac{1}{\omega - J_1}), \tag{12}$$

where

$$\rho_1 = \frac{e^{(J_1/4k_BT)}}{3e^{(J_1/4k_BT)} + e^{(-3J_1/4k_BT)}}, \quad \rho_2 = \frac{e^{(-3J_1/4k_BT)}}{3e^{(J_1/4k_BT)} + e^{(-3J_1/4k_BT)}}. \tag{13}$$

Performing the spatial Fourier transformation of eq.(9) and (10), and then solving the resultant equations with respect to $< S_{q,1}^{+} >$ and $< S_{q,2}^{+} >$ we obtain

$$\begin{aligned}
\begin{bmatrix} < S_{q,1}^{+} > \\ < S_{q,2}^{+} > \end{bmatrix} &= (hh^* - kk^*)^{-1} \times \\
&\begin{bmatrix} h^*\phi_{11}^{+-}(\omega) - k\phi_{12}^{+-}(\omega)e^{-iqc} & h^*\phi_{12}^{+-}(\omega)e^{iqc} - k\phi_{11}^{+-}(\omega) \\ -k^*\phi_{11}^{+-}(\omega) + h\phi_{12}^{+-}(\omega)e^{-iqc} & -k^*\phi_{12}^{+-}(\omega)e^{iqc} + h\phi_{11}^{+-}(\omega) \end{bmatrix} \begin{bmatrix} h_{q,1}^{+}e^{-i\omega t} \\ h_{q,2}^{+}e^{-i\omega t} \end{bmatrix} \\
&\equiv \begin{bmatrix} \chi_{11}^{+-}(q,\omega) & \chi_{12}^{+-}(q,\omega) \\ \chi_{21}^{+-}(q,\omega) & \chi_{22}^{+-}(q,\omega) \end{bmatrix} \begin{bmatrix} h_{q,1}^{+}e^{-i\omega t} \\ h_{q,2}^{+}e^{-i\omega t} \end{bmatrix}
\end{aligned} \tag{14}$$

with

$$\begin{aligned}
&h = 1 + \frac{J_2}{2}(\alpha\phi_{11}^{+-}(\omega) - \phi_{12}^{+-}(\omega)e^{iq(c+c')}), \quad k = \frac{J_2}{2}(-\phi_{11}^{+-}(\omega)e^{-iqc'} + \alpha\phi_{12}^{+-}(\omega)e^{iqc}), \\
&c = \mid R_{i,1} - R_{i,2} \mid, \quad c' = \mid R_{i+1,1} - R_{i,2} \mid .
\end{aligned} \tag{15}$$

Now, we impose the following self-consistency condition to determine the correlation parameter α:

$$< \{S_1^{+}, S_1^{-}\} > = \frac{1}{N}\sum_q \frac{1}{\pi}\int_{-\infty}^{\infty} d\omega \coth(\frac{\beta\omega}{2})\ \mathrm{Im}\chi_{11}^{+-}(q, \omega + is). \tag{16}$$

Here $< \{S_1^{+}, S_1^{-}\} > = < S_1^{+}S_1^{-} + S_1^{-}S_1^{+} >$ represents the on-site spin correlation calculated by using the effective pair-spin Hamiltonian eq.(3), and in the paramagnetic state we have $< \{S_1^{+}, S_1^{-}\} > = \frac{4}{3}S(S+1) = 1$ for $S{=}1/2$. The implication of the above self-consistency condition is that the on-site spin correlation calculated from the dynamical susceptibility (the right-hand side of eq.(16)) should be equal to that calculated from the effective pair-spin Hamiltonian. It is noted that the self-consistency equation constructed by using $\chi_{22}^{+-}(q,\omega)$ gives the same results.

STATIC SUSCEPTIBILITY AND MAGNETIC EXCITATION

Once the correlation parameter α is determined self-consistently, the form of the dynamical susceptibility tensor $\tilde{\chi}^{+-}(q,\omega)$ of the paramagnetic state is fixed and then we calculate various physical quantities from $\tilde{\chi}^{+-}(q,\omega)$. First, the static magnetic susceptibility per unit cell $\chi(T)$ is obtained as follows:

$$\begin{aligned}\chi(T) &= \frac{1}{2}(\chi_{11}^{+-}(0,0)+\chi_{12}^{+-}(0,0)+\chi_{21}^{+-}(0,0)+\chi_{22}^{+-}(0,0)) \\ &= \frac{4}{k_{\rm B}T\{3+\exp(\frac{|J_1|}{k_{\rm B}T})\}+J_2(\alpha-1)}. \end{aligned} \tag{17}$$

Secondly, the energy of magnetic excitation $\omega(q)$ is obtained from the pole of the dynamical susceptibility $\chi_{ij}^{+-}(q,\omega)$ and it is expressed as

$$\omega(q) = |J_1|\sqrt{1+\frac{J_2}{J_1}(\rho_1-\rho_2)\{\alpha+\cos q(c+c')\}}. \tag{18}$$

We have performed numerical calculations for several values of $a \equiv J_2/\mid J_1 \mid$. The value of α determined self-consistently from eq.(16) exhibits a characteristic temperature dependence. First, α takes positive values less than one and is vanishing at $T=\infty$. With decreasing temperature from high temperatures α increases monotonically and presents a maximum around the temperature corresponding to about $0.3|J_1|$. Finally α approaches to some finite value toward T=0 K.

In Fig. 1(a) we show the static magnetic susceptibility calculated by the Pair-DCEFA as a function of temperature for several values of a. In the vicinity of T=0 K $\chi(T)$ behaves as $\chi(T) \approx \frac{4}{k_{\rm B}T\exp(\frac{|J_1|}{k_{\rm B}T})}$ and hence $\chi(T)$ vanishes at T=0 K, which is consistent with the fact that in the AF-F chain there is a gap between the singlet ground state and the excited states.[4] With increasing temperature from zero $\chi(T)$ increases rapidly and shows a broad maximum around the temperature corresponding to $(0.6 \sim 0.7)|J_1|$, and finally it approaches to zero towards $T=\infty$. The dotted curves in Fig. 1(a) represent $\chi(T)$ calculated by the EDM for 14 spins.[1] $\chi(T)$ obtained by the Pair-DCEFA agrees fairly well with the results of the EDM.

In Fig. 1(b) we show the dispersion of the magnetic excitation $\omega(q)$ calculated at T=0 K for several values of a. Reflecting the existence of the gap between the ground state and the excited states the value of $\omega(q)$ is finite for any q, and it exhibits a minimum at $q=\pm\pi/2$. This makes a striking contrast with the AF alternating chains in which $\omega(q)$ has a minimum at $q=0$ and $q=\pi$. The magnetic excitation can be observable by inelastic neutron scattering measurements. At T=0 K the scattering intensity $S(q,\omega(q))$ is calculated from $S(q,\omega(q)) = \mathrm{Im}(\chi_{11}^{+-}(q,\omega(q)) + \chi_{12}^{+-}(q,\omega(q)) + \chi_{21}^{+-}(q,\omega(q)) + \chi_{22}^{+-}(q,\omega(q)))$, and we obtain

$$S(q,\omega(q)) \propto \frac{|J_1|}{\omega(q)}\{1-\cos(qc)\}. \tag{19}$$

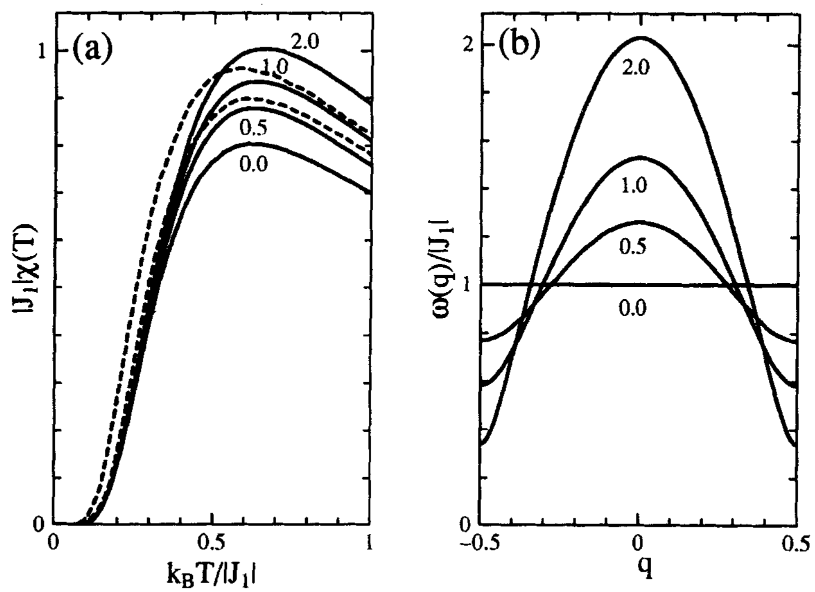

FIGURE 1 (a) The static magnetic susceptibility $\chi(T)$ per unit cell and (b) the magnetic excitation $\omega(q)$ calculated by the Pair-DCEFA for $a \equiv J_2/|J_1|$ = 0.0, 0.5, 1.0 and 2.0. The dotted curves for a=0.5 and 1.0 in (a) represent the results obtained by the EDM.[1] The unit of q in (b) is $2\pi/(c+c')$.

APPLICATION TO Cu(TIM)CuCl$_4$ AND [Cu(bpym)(OH)$_2$]$\cdot$2H$_2$O

Recently S=1/2 AF-F alternating chains have been discovered in organic materials. Examples are Cu(TIM)CuCl$_4$ and [Cu(bpym)(OH)$_2$]$\cdot$2H$_2$O.[1] The observed susceptibilities of Cu(TIM)CuCl$_4$ and [Cu(bpym)(OH)$_2$]$\cdot$2H$_2$O are shown by the open circles in Figs. 2(a) and 3(a), respectively. We have analysed the observed susceptibilities by our Pair-DCEFA and estimated the exchange couplings in these two systems. The results are J_1=−6.5 K and J_2=13.0 K (a=2.0) for Cu(TIM)CuCl$_4$; and J_1=−192.5 K and J_2=144.4 K (a=0.75) for [Cu(bpym)(OH)$_2$]$\cdot$2H$_2$O. The susceptibilities calculated by the Pair-DCEFA with use of these exchange couplings are shown by full curves in Figs. 2(a) and (b). The agreement between the experimental and the theoretical results is satisfactory. The values of exchange coupling estimated by us are almost the same as those evaluated in Ref. 1 for $[Cu(bpym)(OH)_2]\cdot 2H_2O$ ($J_1=-200$ K, $a=0.75$), but a little bit different from those in Ref. 1 for $Cu(TIM)CuCl_4$ ($J_1=-7.5$ K, $a=3.0$).

We have calculated also the magnetic excitation and the inelastic neutron scattering intensity for $Cu(TIM)CuCl_4$ and $[Cu(bpym)(OH)_2]\cdot 2H_2O$ with use of the exchange integrals determined above. The results are shown in Figs. 3(a) and (b). Since the value of $S(q, \omega(q))$ depends on the lattice parameters c and c', we have used the following values of c and c' in the actual calculations: c=4.737 Å and c'=4.227 Å for $Cu(TIM)CuCl_4$[5] and c=5.451 Å and c'=2.886 Å for $[Cu(bpym)(OH)_2]\cdot 2H_2O$.[6] The inelastic neutron scattering measurements in these systems are desired.

Quite recently specific heat measurements have been done for $Cu(TIM)CuCl_4$ and a phase transition has been observed at about 1 K.[7] This result may indicate the importance of the interchain coupling. We are now investigating the effect of interchain coupling, and the results will be reported elsewhere.

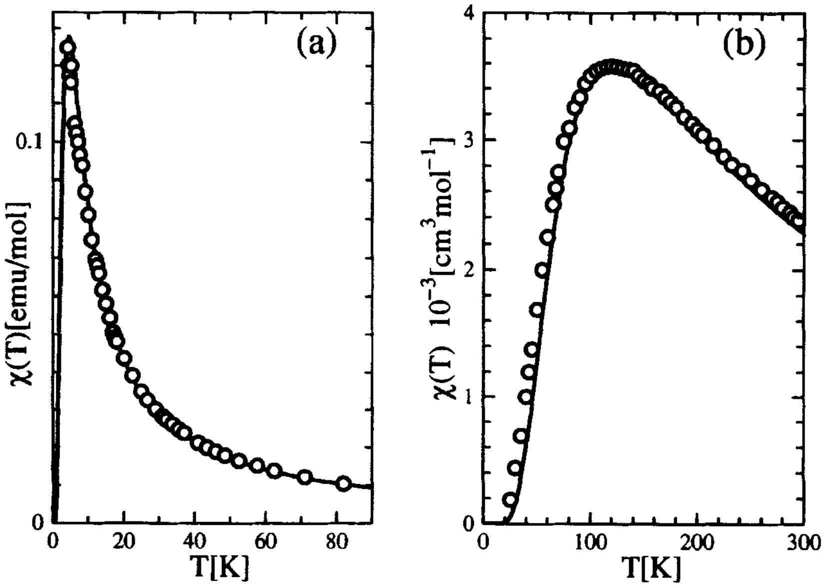

FIGURE 2 The static magnetic susceptibility $\chi(T)$ calculated by the Pair-DCEFA: (a) $Cu(TIM)CuCl_4$ ($J_1=-6.5$ K, $J_2=13.0$ K, $a=2.0$) and (b) $[Cu(bpym)(OH)_2]\cdot 2H_2O$ ($J_1=-192.5$ K, $J_2=144.4$ K, $a=0.75$). The open circles denote the experimental data.[1]

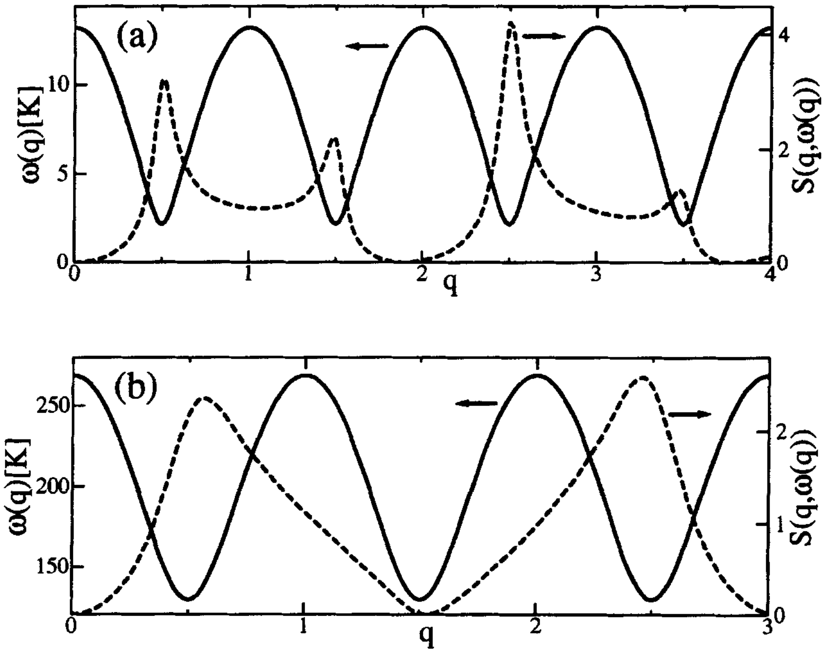

FIGURE 3 The magnetic excitation $\omega(q)$ (full curve) and its neutron scattering intensity $S(q,\omega(q))$ (dotted curve) at T=0 K: (a) Cu(TIM)CuCl$_4$ and (b) [Cu(bpym)(OH)$_2$]$\cdot$2H$_2$O. The unit of intensity is arbitrary and the unit of q is $2\pi/(c+c')$.

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