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THEORETICAL STUDY ON ORGANIC ONE-DIMENSIONAL FERRIMAGNETS

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Abstract The magnetic susceptibility $\chi(T)$ of one-dimensional ferrimagnets consisting of two kinds of quantum spins $\boldsymbol{S}_1$ and $\boldsymbol{S}_2$ are calculated by the dynamical correlated-effective-field approximation (DCEFA). At high temperatures $\chi(T)$ obeys the Curie–Weiss law with a negative Weiss temperature. As the temperature is decreased, $\chi(T)$ diverges towards T=0 K according to $\chi(T) \cong \frac{4(g\mu_B)^2}{9|J|}\sqrt{X_1X_2}(\sqrt{X_1}-\sqrt{X_2})^2(\frac{|J|}{k_BT})^2$ with X_1=$S_1(S_1+1)$ and X_2=$S_2(S_2+1)$. $\chi(T)$ has been calculated also by the exact diagonalization method (EDM) for the case of S_1=1 and S_2=1/2. It is found that $\chi(T)$ obtained by the DCEFA agrees well with that obtained by the EDM in the whole temperature range. The observed susceptibility of an organic one-dimensional ferrimagnet Mn(II)(hfac)$_2$(dipycarbene) (S_1=5/2 and S_2=1 system) has been analysed by DCEFA and the exchange coupling is estimated to be −15 K.

INTRODUCTION

In the last two decades chemists have discovered new classes of low dimensional magnetic systems which are quite interesting from a physical point of view. Examples are spin Peierls systems,[1] Haldane systems[2] and antiferromagnetic–ferromagnetic alternating chains.[3] Furthermore, organic one-dimensional ferrimagnets have been synthesized recently,[4] but there is no theoretical work on their magnetic properties except the calculation of magnetic susceptibility on the basis of the classical spin model.[5]

In this paper we apply the dynamical correlated-effective-field approximation (DCEFA)[6] to calculate the magnetic susceptibility $\chi(T)$ of one-dimensional ferrimagnets consisting of two kinds of quantum spins $\boldsymbol{S}_1$ and $\boldsymbol{S}_2$. The advantages of 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 without difficulty. Thirdly it can treat easily complicated magnetic systems, for example, systems whose unit cell contains many kinds of spins. To confirm the validity and the usefulness of the DCEFA we have calculated $\chi(T)$ also

by the exact diagonalization method for the case of S_1=1 and S_2=1/2. Finally we analyse the observed susceptibility[4] of an organic one-dimensional ferrimagnet Mn(II)(hfac)$_2$(dipycarbene) in which S_1=5/2 and S_2=1 spins linearly align alternatingly and the nearest neighboring exchange coupling is antiferromagnetic.

DYNAMICAL CORRELATED-EFFECTIVE-FIELD APPROXIMATION

We consider a linear-chain spin system whose unit cell contains two spins with different spin values, S_1 and S_2. We express the Hamiltonian as follows:

$$\mathcal{H} = -\sum_{ij}\sum_{mn} J_{ij}^{mn} \boldsymbol{S}_{im} \cdot \boldsymbol{S}_{jn} , \tag{1}$$

where i and j denote the unit cell number, m and n (=1 or 2) specify the spins in a unit cell, and J_{ij}^{mn} is the exchange coupling. The essence of the DCEFA lies in approximating the spin product $S_{im}S_{jn}$ as

$$S_{im}(< S_{jn} > -\alpha_m < S_{im} >) + S_{jn}(< S_{im} > -\alpha_n < S_{jn} >),$$

where α_m (m=1,2) denotes correlation parameters, and $< S_{im} >$ and $< S_{jn} >$ represent the spontaneous spin moments or the spin moments induced by external fields. Since there are two kinds of spins in a unit cell, we have introduced two correlation parameters α_1 and α_2, which can be determined from self-consistency condition required from the fluctuation-dissipation theorem.

To calculate the wave-vector (q) dependent susceptibility within the DCEFA we apply the q dependent fictitious external-field h_{qm} along the z-axis. We adopt the decoupling procedure described above, and then within the linear responce we obtain the following relations between the external field and the Fourier component of the field-induced spin moments:

$$\langle S_{q1}^z \rangle = \phi_1 \left[2\left(J_q^{11} \langle S_{q1}^z \rangle - \alpha_1 J_0^{11} \langle S_{q1}^z \rangle \right) + 2\left(J_q^{12} \langle S_{q2}^z \rangle - \alpha_1 J_0^{12} \langle S_{q1}^z \rangle \right) + h_{q1} \right], \tag{2}$$

$$\langle S_{q2}^z \rangle = \phi_2 \left[2\left(J_q^{22} \langle S_{q2}^z \rangle - \alpha_2 J_0^{22} \langle S_{q2}^z \rangle \right) + 2\left(J_q^{21} \langle S_{q1}^z \rangle - \alpha_2 J_0^{21} \langle S_{q2}^z \rangle \right) + h_{q2} \right]. \tag{3}$$

Here $\langle S_{qm}^z \rangle$ denotes the thermal average of the spin moments induced by the external fields, J_q^{mn} represents the Fourier transform of the exchange coupling, and $\phi_m \equiv \frac{S_m(S_m+1)}{3k_BT}$ is the susceptibility of a single spin.

Solving eqs.(2) and (3) with respect to $\langle S_{q1}^z \rangle$ and $\langle S_{q2}^z \rangle$ we obtain

$$\begin{pmatrix} \langle S_{q1}^z \rangle \\ \langle S_{q2}^z \rangle \end{pmatrix} = \begin{pmatrix} \chi_{11}(q) & \chi_{12}(q) \\ \chi_{21}(q) & \chi_{22}(q) \end{pmatrix} \begin{pmatrix} h_{q1} \\ h_{q2} \end{pmatrix}. \tag{4}$$

Each componet $\chi_{mn}(q)$ of the spin susceptibility tensor is expressed as follows:

$$\chi_{11}(q) = \frac{\phi_1\left[1-2\phi_2\left\{J_q^{22}-\alpha_2\left(J_0^{22}+J_0^{21}\right)\right\}\right]}{Det}, \tag{5}$$

$$\chi_{22}(q) = \frac{\phi_2\left[1-2\phi_1\left\{J_q^{11}-\alpha_1\left(J_0^{11}+J_0^{12}\right)\right\}\right]}{Det}, \tag{6}$$

$$\chi_{12}(q) = \frac{2\phi_1\phi_2 J_q^{12}}{Det}, \quad \chi_{21}(q) = \frac{2\phi_1\phi_2 J_q^{21}}{Det}, \tag{7}$$

with

$$\begin{aligned} Det &= \left[1-2\phi_1\left\{J_q^{11}-\alpha_1\left(J_0^{11}+J_0^{12}\right)\right\}\right]\left[1-2\phi_2\left\{J_q^{22}-\alpha_2\left(J_0^{22}+J_0^{21}\right)\right\}\right] \\ &\quad -4\phi_1\phi_2 J_q^{12}J_q^{21}. \end{aligned} \tag{8}$$

The uniform magnetic susceptibility per unit cell $\chi(T)$ is expressed as

$$\chi(T) = \mu_B^2\left[g_1^2\chi_{11}(0) + g_1g_2\chi_{12}(0) + g_1g_2\chi_{21}(0) + g_2^2\chi_{22}(0)\right], \tag{9}$$

where g_1 and g_2 denote the g-values of $\boldsymbol{S}_1$ and $\boldsymbol{S}_2$, respectively.

The correlation parameters α_m can be determined from the condition that the on-site correlation $< \{S_{im}^z, S_{im}^z\} >$ calculated from the susceptibility $\chi_{mm}(q)$ should be equal to $\frac{2}{3}S_m(S_m+1)$.[6] The self-consistency condition is explicitly expressed as

$$\frac{1}{N}\sum_q \frac{1-2\phi_1\left\{J_q^{11}-\alpha_1\left(J_0^{11}+J_0^{12}\right)\right\}}{Det} = 1, \tag{10}$$

$$\frac{1}{N}\sum_q \frac{1-2\phi_2\left\{J_q^{22}-\alpha_2\left(J_0^{22}+J_0^{21}\right)\right\}}{Det} = 1. \tag{11}$$

If we consider only the nearest-neighboring exchange coupling J (<0),

$$J_q^{11} = J_q^{22} = 0 \quad \text{and} \quad J_q^{12} = J_q^{21} = 2J\cos qa, \tag{12}$$

where a denotes the distance between the nearest-neighboring spins. Then, α_1 and α_2 are determined analytically from eqs.(11) and (12) as follows:

$$\alpha_1 = \frac{3t}{4X_1} - \sqrt{\frac{X_2}{X_1} + \left(\frac{3t}{4X_1}\right)^2}, \tag{13}$$

$$\alpha_2 = \frac{3t}{4X_2} - \sqrt{\frac{X_1}{X_2} + \left(\frac{3t}{4X_2}\right)^2}. \tag{14}$$

with $X_1=S_1(S_1+1)$, $X_2=S_2(S_2+1)$ and $t \equiv \frac{k_B T}{|J|}$. If we assume $g_1 = g_2 \equiv g$, the uniform magnetic susceptibility is expressed in a simple form as follows:

$$\chi(T) = \frac{(g\mu_B)^2}{|J|} \frac{4X_1X_2}{9t^2} \left[\sqrt{\frac{X_2}{X_1} + \left(\frac{3t}{4X_1}\right)^2} + \sqrt{\frac{X_1}{X_2} + \left(\frac{3t}{4X_2}\right)^2} - 2 \right]. \tag{15}$$

At high temperature $\chi(T)$ obeys the Curie-Weiss law

$$\chi(T) = \frac{(g\mu_B)^2}{|J|} \frac{X_1 + X_2}{3} \left[t + \frac{8X_1X_2}{3(X_1+X_2)} \right]^{-1}, \tag{16}$$

and at low temperatures near T=0 K it behaves as

$$\chi(T) = \frac{4(g\mu_B)^2}{9|J|} \sqrt{X_1X_2} (\sqrt{X_1} - \sqrt{X_2})^2 t^{-2}. \tag{17}$$

In Fig. 1 we show $\chi(T)$ calculated as a function of T for S_1=1 and S_2=1/2.

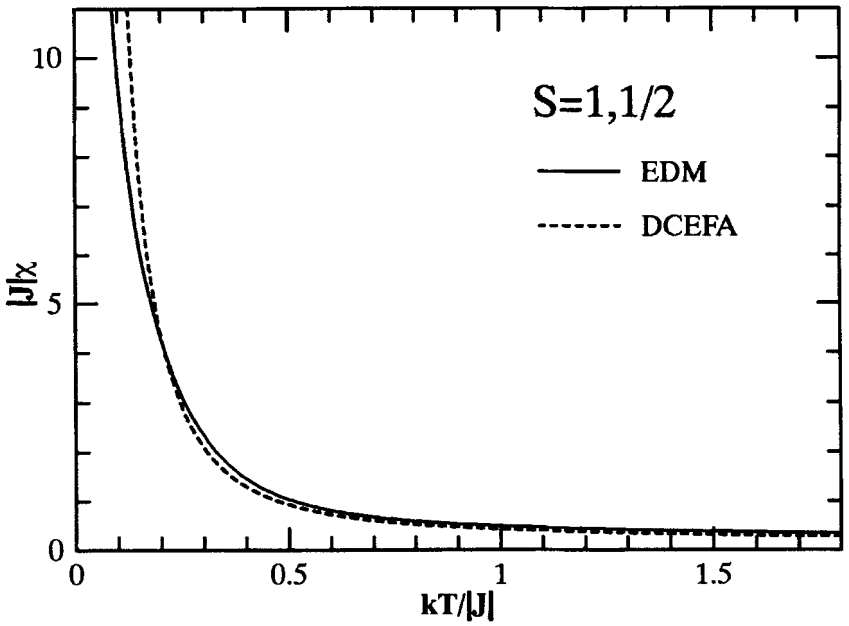

FIGURE 1 The uniform magnetic susceptibility $\chi(T)$ per unit cell calculated for S_1=1 and S_2=1/2 ferrimagnet. The full (dotted) line represents the result obtained by DCEFA (EDM).

To confirm the validity and the usefulness of the DCEFA we have calculated $\chi(T)$ also by the exact diagonalization method (EDM) for the case of S_1=1 and S_2=1/2. Actual calculations have been done for the chain size up to six unit cells

(twelve spins) and the values of $\chi(T)$ of the infinite-size chain have been evaluated by $1/N$-plot. The values of $\chi(T)$ obtained by the EDM are plotted by the dotted line in Fig. 1. As seen from the figure the susceptibility obtained by the DCEFA agrees fairly well with that obtained by the EDM for the whole temperature range.

APPLICATION TO Mn(II)(hfac)$_2$(dipycarbene)

Recently Koga *et al.*[4] have measured the magnetic susceptibility of organic system Mn(II)(hfac)$_2$(dipycarbene) which can be regarded as a one-dimensional ferrimagnet consisting of two kinds of spins S_1=5/2 and S_2=1. The observed susceptibility shows certainly temperature dependence characteristic to one-dimensional ferrimagnets as described in the previous section. In Fig. 2 the diamonds show the experimental values of χT, *i.e.* product of susceptibility and temperature. At high temperatures the value of χT is close to $\frac{(g\mu_B)^2}{3k_B}[S_1(S_1+1)+S_2(S_2+1)]$. As the temperature is lowered from high temperature, χT decreases slightly at first, and with further decreasing temperature it turns to increase and seems to diverge toward T=0 K.

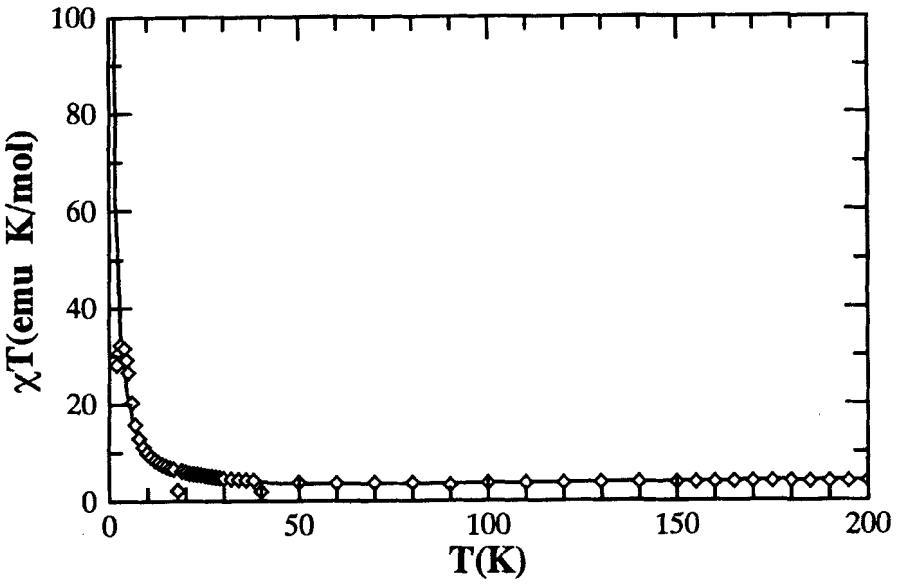

FIGURE 2 The χT-plot (product of unifrom magnetic susceptibility and temperature) of Mn(II)(hfac)$_2$(dipycarbene) (S_1=5/2 and S_2=1 system). The diamonds denote the experimental data[4] and the full line shows the theoretical results obtained by DCEFA with use of J=−15 K.

We have tried to determine the nearest-neighboring exchange coupling J in Mn(II)(hfac)$_2$(dipycarbene) by analysing the observed susceptibility using the results obtained by the DCEFA in the previous section. As result it is found that the observed susceptibility is well reproduced by assuming $J = -15$ K and $g_1 = g_2 = 2$. In Fig. 2 the full line represents the theoretical χT-plot. Agreement between the experimental and the theoretical results is quite excellent.

In this paper we have derived the general expression of the uniform magnetic susceptibility of one-dimensional ferrimagnets on the basis of the DCEFA. It is confirmed that the results of DCEFA agree well with those of EDM. Actual calculations based on the DCEFA have been restricted to the case of nearest neighboring exchange interaction, but it is easily extended to the system with far neighboring exchange coupling. It can be applied without difficulty also to three dimensional systems. The exchange coupling of the one-dimensional ferrimagnet Mn(II)(hfac)$_2$(dipycarbene) (S_1=5/2 and S_2=1) has been estimated to be $J = -15$ K. Recently Drillon and Rabu have obtained a value of $J = -17 \sim -19$ K on the basis of a method similar to the one described in Ref. 5.[7]

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