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Monte Carlo study of a mixed spin-2 and spin-5/2 Ising system on a honeycomb lattice

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Abstract. In order to study the magnetic properties of a mixed spin-2 and spin-5/2 ferrimagnetic Ising system on a two-dimensional honeycomb lattice, we carried out Monte Carlo simulations. We found that the system which includes only a nearest-neighbour interaction and a single-ion anisotropy just on a spin-2 does not have a compensation point. The result contradicts that predicted by the effective-field theory. The inconsistency arises from how one estimates the two-point and three-point correlations.

1. Introduction

Intensive experimental work is currently being carried out in which stable crystalline magnets with spontaneous moments at room temperature are synthesized [1]. Among such materials, many bimetallic molecule-based magnetic materials have exhibited ferrimagnetic properties and seem to be well interpreted with a model of mixed spins [2]. In a ferrimagnetic material, the different temperature dependences of the sublattice magnetizations raise the possibility of the existence of a compensation temperature: a temperature below the critical point where the total magnetization is zero [3]. This interesting behaviour has important applications in the field of thermomagnetic recording [4, 5]

Recently the molecular magnetic materials $AFe^{II}Fe^{III}(C_2O_4)_3$ ($A = N(n\text{-}C_nH_{2n+1})_4$, $n = 3$–5) have been synthesized and they have critical temperatures between 35 and 48 K [6]. They have a honeycomb structure in which $Fe^{II}(S = 5/2)$ and $Fe^{III}(S = 2)$ occupy sites alternately. All nearest-neighbour Fe^{II} and Fe^{III} pairs are bridged by C_2O_4 and cations A are arranged between honeycomb layers. It is reported that there exists a compensation point for some cations. In order to explain the behaviour, a system which is modelled with the Hamiltonian

$$H = -J \sum_{(ij)} S_i \sigma_j - D \sum_j (\sigma_j)^2 \tag{1}$$

was investigated on the basis of effective-field theory (EFT) with correlations [7], where S_i and σ_i are spin-5/2 and spin-2 respectively. J (<0) is an exchange interaction and the summation $\sum_{(ij)}$ is performed for nearest-neighbour spin pairs. From the study, it was found that a single-ion anisotropy constant D plays an important role as regards the existence of a compensation point and there is a critical value of D above which the compensation point can appear [8]. Note that the system in the theoretical study was a two-dimensional honeycomb lattice, which means that the effects of cations A were neglected.

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In this article, we employ a Monte Carlo simulation as an alternative approach for the same model, equation (1), to investigate the magnetic properties of the system. In section 2 we describe details of our Monte Carlo simulations and the results are shown in section 3. The results are discussed in section 4 and we finally present the conclusions in section 5.

2. The Monte Carlo simulation

We use standard Monte Carlo methods to simulate the Hamiltonian described by equation (1) on a honeycomb lattice with periodic boundary conditions. Our periodic honeycomb lattice is represented in figure 1. There are $2L^2$ sites on this lattice and L is equal to 5 for the figure. We label the ith site S_i ($i = 1, \ldots, 2L^2$). With this labelling, we set S_i with odd i as spin-5/2 and S_i with even i as spin-2. Then the Hamiltonian (1) can be rewritten as

$$H = -J \sum_{i\ (\mathrm{odd})} S_i(S_{i_1} + S_{i_2} + S_{i_3}) - D \sum_{i\ (\mathrm{even})} (S_i)^2 \tag{2}$$

where $\sum_{i\ (\mathrm{odd})}$ means summation over only odd i and $\sum_{i\ (\mathrm{even})}$ summation over only even i, and S_{i_k} ($k = 1, 2, 3$) are nearest neighbours of S_i. We chose $L = 50$ for the simulations. Configurations are generated by sequentially sweeping through the lattice and making single-spin-flip attempts. The flips are accepted or rejected according to the Metropolis algorithm [9]. Data are generated with 10^4 Monte Carlo steps per site after discarding the first 5000 steps per site. The error bars are calculated with a jackknife method [10] by taking all the measurements and grouping them in twenty blocks.

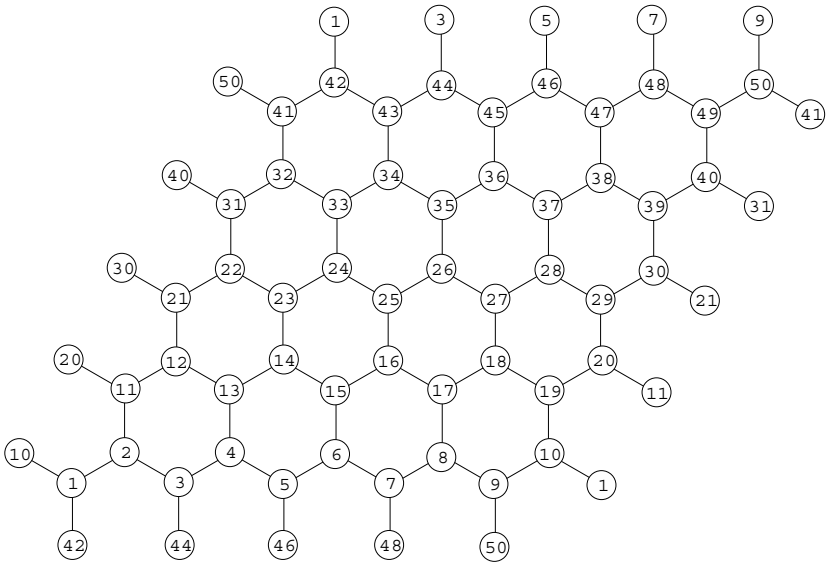

Figure 1. A honeycomb lattice with periodic boundary conditions. The lattice size is $L = 5$ and the number of spins is $2L^2 = 50$ in this example.

We calculate the internal energy per site:

$$E = \frac{\langle H \rangle}{2L^2} \tag{3}$$

the specific heat,

$$\frac{C}{k_{\mathrm{B}}} = \frac{\beta^2}{2L^2}(\langle H^2 \rangle - \langle H \rangle^2) \tag{4}$$

the sublattice magnetizations m_A and m_B defined as

$$m_A = \frac{1}{L^2}\left\langle \sum_{i\ (\mathrm{odd})} S_i \right\rangle \tag{5}$$

and

$$m_B = \frac{1}{L^2}\left\langle \sum_{i\ (\mathrm{even})} S_i \right\rangle \tag{6}$$

and the total magnetization per spin,

$$M = \frac{m_A + m_B}{2} \tag{7}$$

where $\beta = 1/(k_B T)$.

3. Results

Let us start the simulations by calculating the energy per site in order to verify our results. We can calculate the energy of the ground state exactly for the present system. The ground-state energy per site, E_G, is calculated as follows:

$$E_G/|J| = \begin{cases} -\dfrac{15}{2} - 2D/|J| & \text{for } -\dfrac{5}{2} \leqslant D/|J| \\ -\dfrac{15}{4} - \dfrac{1}{2}D/|J| & \text{for } -\dfrac{15}{2} \leqslant D/|J| < -\dfrac{5}{2} \\ 0 & \text{for } D/|J| < -\dfrac{15}{2}. \end{cases} \tag{8}$$

Figure 2 shows the temperature dependences of the energy per site for several values of $D/|J|$. As temperature decreases to zero, each energy approaches the value that we calculated using equation (8). Thus the reliability of our calculations is checked.

In figure 3, we plot total magnetizations M defined by equation (7) as a function of the temperature for several values of $D/|J|$. At first glance, we cannot recognize the existence of the compensation point which was predicted by the effective-field theory [8], contrary to our expectations. The theory predicted that the critical value of the single-ion anisotropy constant above which the compensation point may appear was $D/|J| = 3.349$. However, the compensation point does not appear even for large values of $D/|J|$, say $D/|J| = 8.0$. Even if $D/|J|$ becomes larger than 8.0, the behaviour of the magnetization curve is not affected very much. We did not plot the magnetization curve in the case of $D/|J| = 16.0$, but its behaviour is almost same as that in the case of $D/|J| = 8.0$. It is interesting to see various types of behaviour of the magnetization curves in figure 3. When $D/|J|$ is positive or equal to zero, the magnetization behaves like that of a ferromagnet, which follows a Q-type curve in Néel's classification [3]. The magnetization curve becomes P-type for values of $D/|J|$ lower than zero. $D/|J| = -2.5$ is the critical value and the magnetization behaves as a Q-type one again. The value of the total magnetization is 0.5, which indicates that the ground state is the state where spin-2 takes $S_i = 1$ or $S_i = 2$ with equal probability and spin-5/2 takes $S_i = -5/2$. When $D/|J|$ becomes just less than -2.5, the magnetization decreases rapidly from the maximum value $|M| = 0.75$ reached at low temperature. This behaviour is not predicted in Néel's classification and a similar behaviour has been reported in Monte Carlo simulation of a mixed spin-2 and spin-1/2 Ising ferrimagnetic system [12, 13]. As $D/|J|$ becomes smaller, the shape of the magnetization curve changes from Q-type to P-type.

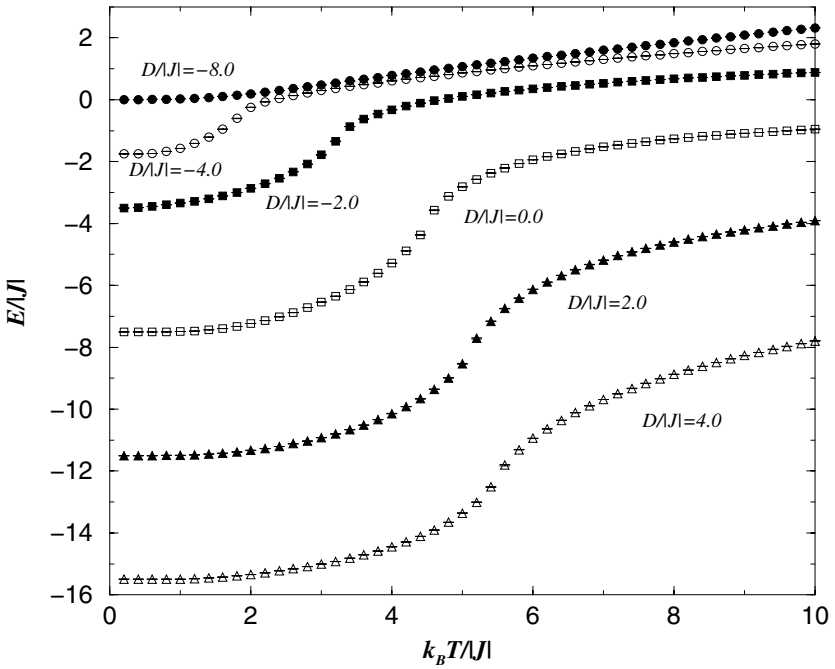

Figure 2. The temperature dependences of the energy per site for several values of $D/|J|$.

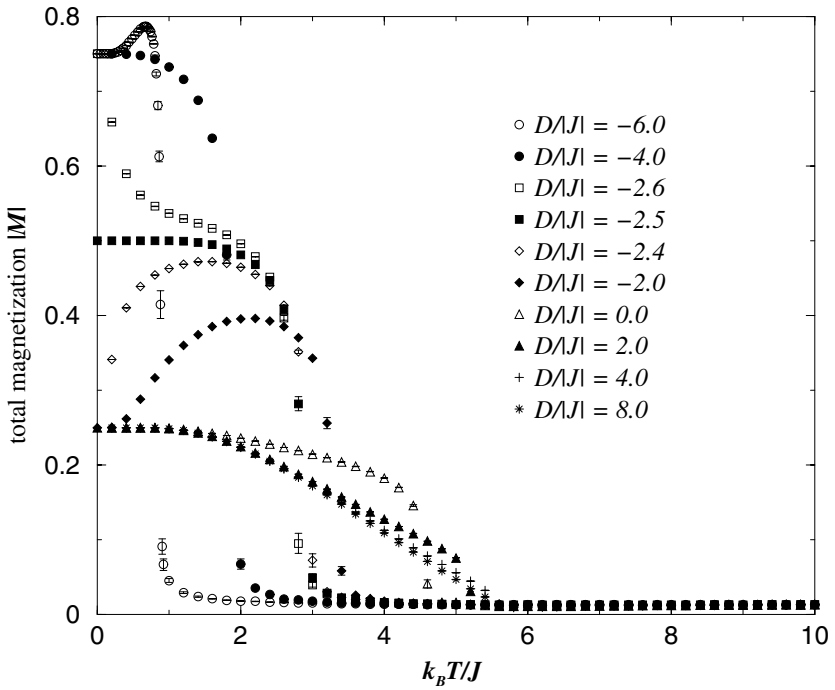

Figure 3. Total magnetization M as a function of temperature for $D/|J| = -6.0, -4.0, -2.6, -2.5, -2.4, -2.0, 0.0, 2.0, 4.0, 8.0$.

As regards other properties, we can see from figure 3 that the critical temperature decreases as $D/|J|$ decreases. Thus in order to investigate how the critical temperature is affected by $D/|J|$, we calculated the specific heats defined by equation (4). T_C is obtained approximately by locating the maxima of the specific heat curve. In figure 4, the specific heat curves are plotted and we show the T_C–$D/|J|$ phase diagram in figure 5, from which we can see the variations of the critical temperature with the change of $D/|J|$. The results obtained from effective-field and mean-field theory [8] are also shown in figure 5 for comparison. The dependences of the compensation temperatures on $D/|J|$ are also plotted for both theories. It is found that our Monte Carlo simulation estimates of the values of the critical temperatures for each $D/|J|$ were lower than those from both theories and there is no branch for compensation temperatures. This kind of disagreement between theories and Monte Carlo simulations is also reported for a similar model [11, 12] and we will discuss the cause of the inconsistency in the next section.

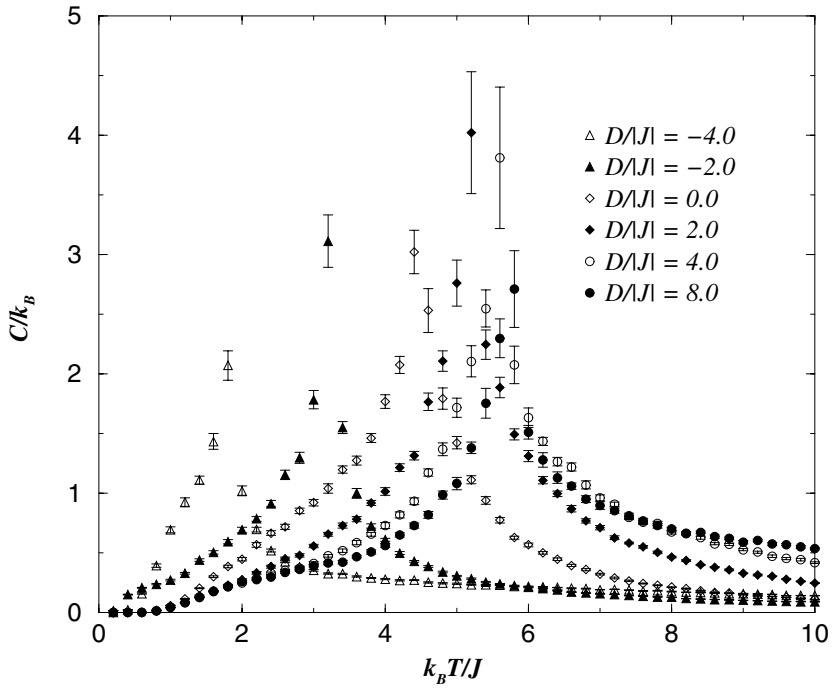

Figure 4. Specific heats against $k_B T/J$ for different values of $D/|J|$.

4. Discussion

Let us consider the inconsistency of results between the theory (EFT) and the Monte Carlo simulation. Our Monte Carlo simulation is a non-perturbative method used to study the system neglecting finite-size effects. However, we could not obtain drastic changes although we carried out simulations with $L = 100$. On the other hand, the decoupling approximation was introduced for treating the multispin correlation function in the EFT, that is, $\langle S_{i_1} S_{i_2} S_{i_3} \rangle \approx \langle S_{i_1} \rangle \langle S_{i_2} \rangle \langle S_{i_3} \rangle$ and $\langle S_{i_k} S_{i_l} \rangle \approx \langle S_{i_k} \rangle \langle S_{i_l} \rangle$ $((k, l) = (1, 2), (2, 3), (3, 1))$, where i_k $(k = 1, 2, 3)$ are nearest neighbours of S_i. Therefore it may be useful to calculate multispin correlation functions in the simulation. Let us define two-spin and three-spin correlation

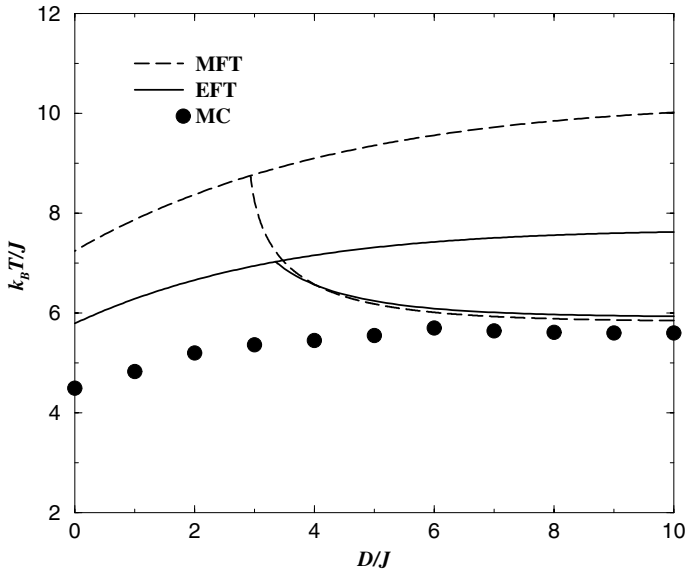

Figure 5. The transition temperature and the compensation temperature as functions of $D/|J|$. Points, the solid line and the dashed line are the results from the present Monte Carlo simulation, the effective-field theory (EFT) and the mean-field theory (MFT) respectively.

functions as follows:

$$G^{(2)}(i_k, i_l) = \langle S_{i_k} S_{i_l} \rangle - \langle S_{i_k} \rangle \langle S_{i_l} \rangle \tag{9}$$

and

$$G^{(3)}(i_1, i_2, i_3) = \langle S_{i_1} S_{i_2} S_{i_3} \rangle - \langle S_{i_1} \rangle \langle S_{i_2} \rangle \langle S_{i_3} \rangle \tag{10}$$

respectively. Furthermore, we define $G_\alpha^{(2)}$ and $G_\alpha^{(3)}$ by averaging $G^{(2)}(i_k, i_l)$ and $G^{(3)}(i_1, i_2, i_3)$ over the whole lattice for all pairs of spins, where α is A (spin-5/2) or B (spin-2). $G_\alpha^{(2)}$ and $G_\alpha^{(3)}$ are calculated to be

$$\begin{aligned} G_{\mathrm{A}}^{(2)} &= \frac{1}{L^2} \sum_{i\ (\mathrm{even})} \frac{G^{(2)}(i_1, i_2) + G^{(2)}(i_2, i_3) + G^{(2)}(i_3, i_1)}{3} \\ G_{\mathrm{B}}^{(2)} &= \frac{1}{L^2} \sum_{i\ (\mathrm{odd})} \frac{G^{(2)}(i_1, i_2) + G^{(2)}(i_2, i_3) + G^{(2)}(i_3, i_1)}{3} \end{aligned} \tag{11}$$

and

$$\begin{aligned} G_{\mathrm{A}}^{(3)} &= \frac{1}{L^2} \sum_{i\ (\mathrm{even})} G^{(3)}(i_1, i_2, i_3) \\ G_{\mathrm{B}}^{(3)} &= \frac{1}{L^2} \sum_{i\ (\mathrm{odd})} G^{(3)}(i_1, i_2, i_3). \end{aligned} \tag{12}$$

In figure 6 we plot $G_{\mathrm{A}}^{(2)}$, $G_{\mathrm{B}}^{(2)}$, $G_{\mathrm{A}}^{(3)}$ and $G_{\mathrm{B}}^{(3)}$ with curves showing the magnetization m_{A} obtained from the Monte Carlo simulation and the effective-field theory for $D/|J| = 8.0$. We see from this figure that the larger the correlations become, the larger the gap between the simulation and the theory becomes. In particular, the correlations and the gap are largest near the critical temperature.

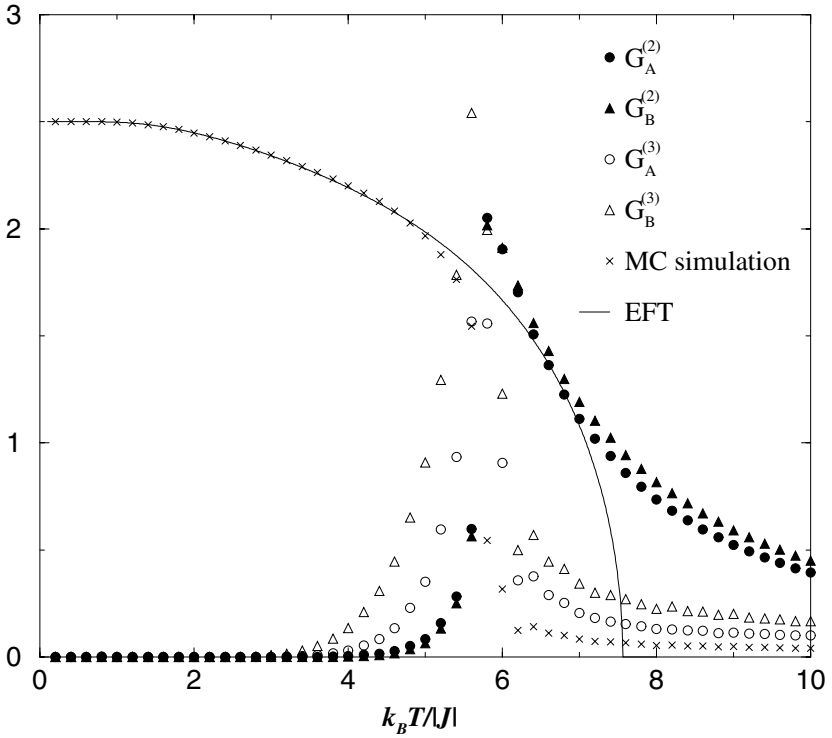

Figure 6. Dependences of the two-spin and three-spin correlation functions on temperature. Curves showing the magnetization m_A obtained from Monte Carlo simulation and the effective-field theory (EFT) are also plotted.

5. Conclusions

We have applied a Monte Carlo simulation to the study of a mixed spin-5/2 and spin-2 Ising model on a honeycomb lattice modelled by equation (1) in order to investigate a characteristic feature of $AFe^{II}Fe^{III}(C_2O_4)_3$ ($A = N(n\text{-}C_nH_{2n+1})_4$, $n = 3$–5). In particular, we have examined the effect of a single-ion anisotropy on the behaviour of the temperature dependence of the magnetization curves and on the critical temperature.

As is seen from figure 3, the system shows a strong dependence on the parameter $D/|J|$ at low temperature, especially for $D/|J|$ near critical values: $D/|J| = 0.0, -2.5$. For $D/|J|$ just below the critical value $D/|J| = -2.5$, the total magnetization curve reveals a peculiar shape at low temperature—that is, the magnetization curve exhibits a rapid drop from its zero-temperature value. As for the existence of compensation points predicted by the effective-field theory and the mean-field theory, we could not find any evidence to support the predictions. The T_C–$D/|J|$ phase diagram calculated is shown in figure 5. T_C estimated from our Monte Carlo simulation is lower than those from both theories. Such results are also reported for a similar model [11–13].

In order to investigate the difference between our results and the theory, we calculated multispin correlation functions $G_A^{(2)}$, $G_B^{(2)}$, $G_A^{(3)}$ and $G_B^{(3)}$ (equations (11), (12)) which were treated with the decoupling approximation in the theories. As $G_\alpha^{(2)}$ and $G_\alpha^{(3)}$ (α is A or B) become large, the difference between the magnetization curves for the theory and the Monte Carlo simulation also becomes large.

In our simulation of the system described by the Hamiltonian (1), we could not find any of the compensation points reported from experiments for the compounds $AFe^{II}Fe^{III}(C_2O_4)_3$ ($A = N(n\text{-}C_nH_{2n+1})_4$, $n = 3$–5) [6]. In the experiment, depending on the nature of the organic cation A, the compound either has a compensation point or not. Therefore, although the interlayer interaction is neglected in the present model Hamiltonian, the system with an interlayer interaction may reveal a compensation point. Furthermore, in the theoretical study, a diluted system is also investigated and an interesting characteristic was reported—that is, several (two or three) compensation points are possible, depending on the single-ion anisotropy and the concentration of atoms. This feature would also be an interesting subject for a simulation.

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