Existence of a compensation temperature of a mixed spin-2 and spin-$\frac{5}{2}$ Ising ferrimagnetic system on a layered honeycomb lattice

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The magnetic properties of a mixed spin-2 and spin-$\frac{5}{2}$ Ising ferrimagnetic system on a layered honeycomb lattice are studied. In particular we investigate the effect of a single-ion anisotropy and an interlayer interaction on the compensation phenomenon, in order to clarify the characteristic features observed in a series of molecular-based magnets $A\mathrm{Fe^{II}Fe^{III}}$ $(\mathrm{C_2O_4})_3[A=\mathrm{N}(n\text{-}\mathrm{C}_n\mathrm{H}_{2n+1})_4, n=3-5]$. We carried out Monte Carlo simulations and found that an interlayer interaction plays one of the roles for the existence of a compensation point. It is pointed out that a compensation point may be possible even if interlayer interactions are zero, provided there are other longer-range interactions.

I. INTRODUCTION

A number of experimental works in the area of molecular-based magnetic materials have been stimulated in recent years and the magnetic properties has become an important focus of scientific interest.[1,2] The search for materials which order at or above room temperature is a major driving force moving the field. Among these materials, ferrimagnets in which two kinds of magnetic atoms regularly alternate antiferromagnetically seem to play an important role. For example, the recently developed amorphous $\mathrm{V(TCNE)}_x \cdot y$ (solvent) order ferrimagnetically as high as 400 K.[3] Another experimental group synthesized compounds such as $A\mathrm{Fe^{II}Fe^{III}}$ $(\mathrm{C_2O_4})_3$ $[A=\mathrm{N}(n\text{-}\mathrm{C}_n\mathrm{H}_{2n+1})_4, n=3-5]$ which have critical temperatures between 35 and 48 K and some of them have compensation temperatures near 30 K,[4] depending on the kind of a cation A^+. The compensation temperature is the temperature where the resultant magnetization vanishes below the critical temperature. The existence of compensation temperatures has important applications in the field of magneto-optic recording.

Mixed Ising systems provide simple models which can show ferrimagnetic ordering and they may have compensation temperatures. The magnetic properties of these models have been studied by several methods such as a mean-field[5] and an effective-field[6] theory, a cluster variational theory,[7] Monte Carlo simulations,[8–10] and so on. Particularly, in relation to compounds $A\mathrm{Fe^{II}Fe^{III}}$ $(\mathrm{C_2O_4})_3$ $[A=\mathrm{N}(n\text{-}\mathrm{C}_n\mathrm{H}_{2n+1})_4, n=3-5]$ mentioned above, there are theoretical[11] and Monte Carlo[12,13] studies in order to examine the magnetic properties with same model Hamiltonian. In the theoretical study on the basis of an effective-field theory (EFT), it is reported that a single-ion anisotropy constant plays an important role for the existence of a compensation point and there is a critical value of a single-ion anisotropy constant above which the compensation point can appear.[11] In the Monte Carlo study, however, there was no evidence to support the theoretical result.[12,13] The series of materials have a layered honeycomb structure, in which $\mathrm{Fe^{II}}$ and $\mathrm{Fe^{III}}$ pairs bridged by oxalate ions $\mathrm{C_2O_4^{2-}}$ are arranged to form a two-dimensional honeycomb structure and cations A^+ are

positioned between layers. However, the system considered in both studies was two-dimensional honeycomb lattice, which means that the effect of a cation A^+, namely an interlayer interaction, was neglected.

In this study, we investigate a mixed spin-2 and spin-$\frac{5}{2}$ Ising ferrimagnetic system on a layered honeycomb lattice with Monte Carlo simulations in order to clarify the characteristic behavior of the molecular-based magnet $A\mathrm{Fe^{II}Fe^{III}}$ $(\mathrm{C_2O_4})_4[A=\mathrm{N}(n\text{-}\mathrm{C}_n\mathrm{H}_{2n+1})_4, n=3-5]$. In particular, the effect of the interlayer interaction is examined. In Sec. II, we describe our model and details of our Monte Carlo simulations and results are shown in Sec. III. We conclude our study in Sec. IV.

II. MODEL AND MONTE CARLO SIMULATIONS

We study a layered honeycomb lattice with spin-2 and spin-$\frac{5}{2}$ spins which represent $\mathrm{Fe^{II}}$ and $\mathrm{Fe^{III}}$ atoms, respectively. Both spins locate in alternating sites of a two-dimensional honeycomb lattice and the lattice has a layered structure. The Hamiltonian we adopt has the form

$$H = -J_1 \sum_l \sum_{(ij)} S_i^{(l)} \sigma_j^{(l)} - J_2 \sum_l \sum_j \sigma_j^{(l)} \sigma_j^{(l+1)} - D \sum_l \sum_j (\sigma_j^{(l)})^2, \tag{1}$$

where $S_i^{(l)}$ and $\sigma_j^{(l)}$ spins are spin-$\frac{5}{2}$ and spin-2 ones, respectively, on the lth layer. $J_1(<0)$ is an exchange interaction between $S_i^{(l)}$ and $\sigma_j^{(l)}$, and $J_2(>0)$ is an interlayer interaction between $\sigma_j^{(l)}$ and $\sigma_j^{(l+1)}$. The summation $\Sigma_{(ij)}$ is performed for nearest-neighbor spin pairs.

We apply a standard importance sampling method to simulate the Hamiltonian described by Eq. (1). Each layer of our lattice has a honeycomb structure with a periodic boundary condition represented in Fig. 1, where open and filled circles are $\mathrm{Fe^{II}}$ and $\mathrm{Fe^{III}}$. An unit cell of each layer (indicated by a dotted line in the figure) consists of two atoms and is repeated along the directions a_1 and a_2. $2N^2$ sites are contained in each layer and $2N^2L$ for L layer systems. We chose $N=20$ and $L=20$ for simulations. Configurations are gener-
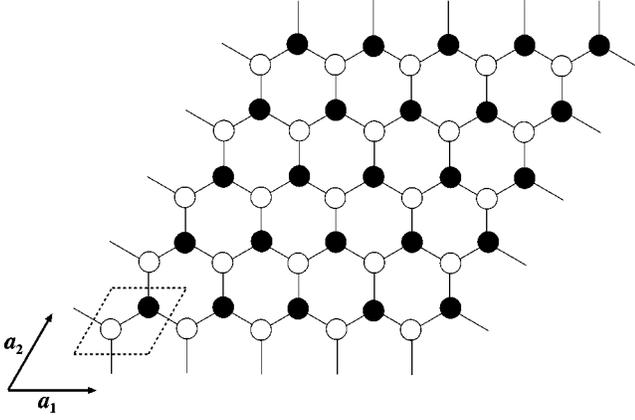
FIG. 1. A selected honeycomb layer with periodic boundary condition. The unit cell consists of two atoms. In this figure the lattice size is $N=5$ and the number of spins is $2N^2=50$. There are $2N^2L$ spins in L layered system.

ated by sequentially sweeping through the lattice and making single spin-flip attempts. The flips are accepted or rejected by the Metropolis algorithm.[14] 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[15] by taking all the measurements and grouping them in 20 blocks.

We calculate the internal energy per site,

$$E=\frac{\langle H\rangle}{2N^2L},\qquad(2)$$

the specific heat,

$$\frac{C}{k_{\mathrm{B}}}=\frac{\beta^2}{2N^2L}(\langle H^2\rangle-\langle H\rangle^2),\qquad(3)$$

the sublattice magnetizations m_A and m_B defined as

$$m_A=\frac{1}{L^2N}\left\langle\sum_i S_i\right\rangle\qquad(4)$$

and

$$m_B=\frac{1}{L^2N}\left\langle\sum_j \sigma_j\right\rangle,\qquad(5)$$

and the total magnetization per spin,

$$M=\frac{m_A+m_B}{2},\qquad(6)$$

where $\beta=1/(k_{\mathrm{B}}T)$.

III. RESULTS

We start our simulation by calculating an internal energy. Since the ground-state energy can be exactly calculated, we can check the reliability of our simulation. The ground-state energy per spin, E_G or $e_G\equiv E_G/|J_1|$, is calculated to be

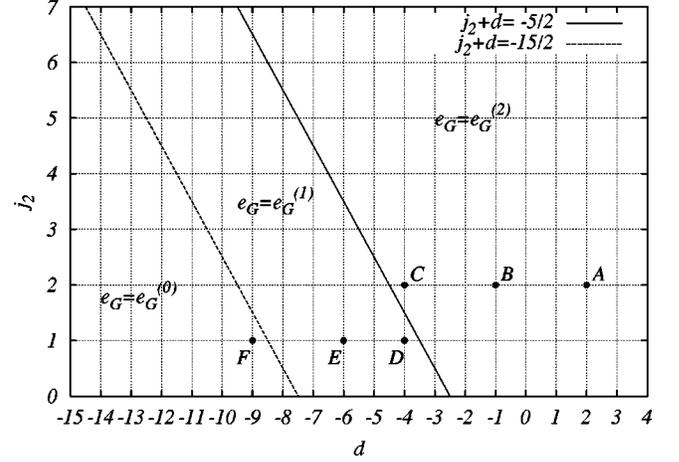$$e_G=e_G^{(2)}\equiv-\frac{15}{2}-2(j_2+d)\ \ \text{for}\ \ -\frac{5}{2}\leqslant j_2+d,$$

FIG. 2. Ground-state diagram of the present model. Six points $(A,\ldots,F)$ are guides for Fig. 3.

$$e_G=e_G^{(1)}\equiv-\frac{15}{4}-\frac{1}{2}(j_2+d)\ \ \text{for}\ \ -\frac{15}{2}\leqslant j_2+d\leqslant-\frac{5}{2},$$

$$(7)$$

$$e_G=e_G^{(0)}\equiv0\ \ \text{for}\ \ j_2+d\leqslant-\frac{15}{2},$$

and Fig. 2 shows the ground-state diagram, where $j_2\equiv J_2/|J_1|$ and $d\equiv D/|J_1|$. Figure 3 shows the temperature dependences of the energy per spin for several sets of values (d,j_2) which are plotted in Fig. 2. As temperature decreases to zero, each energy approaches to the value which are calculated by Eqs. (7).

A. Effects of a single-ion anisotropy

Let us fix the value of j_2 to $j_2=0.2$, and examine the effect of a single-ion anisotropy constant d on the magnetization curve. In Fig. 4, we plot total magnetizations M defined by Eq. (6) as a function of the temperature for several values of d [Fig. 4(a)] and sublattice magnetizations m_A and
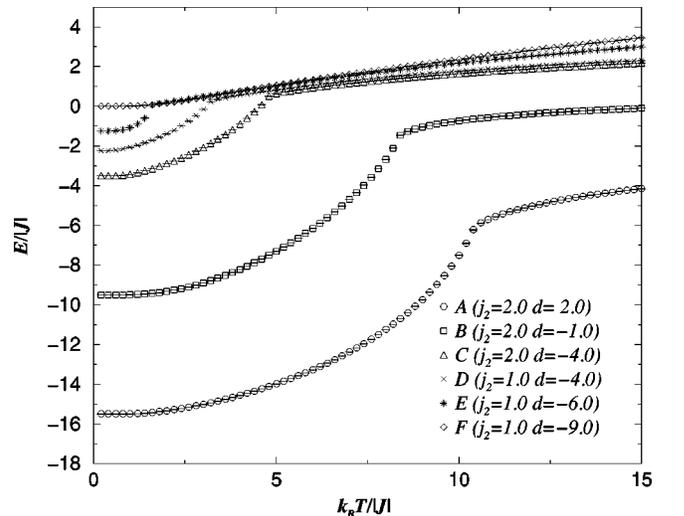

FIG. 3. Temperature dependences of the energy per site for several sets of values (d,j_2). Each set corresponds to one of the points plotted in Fig. 2.
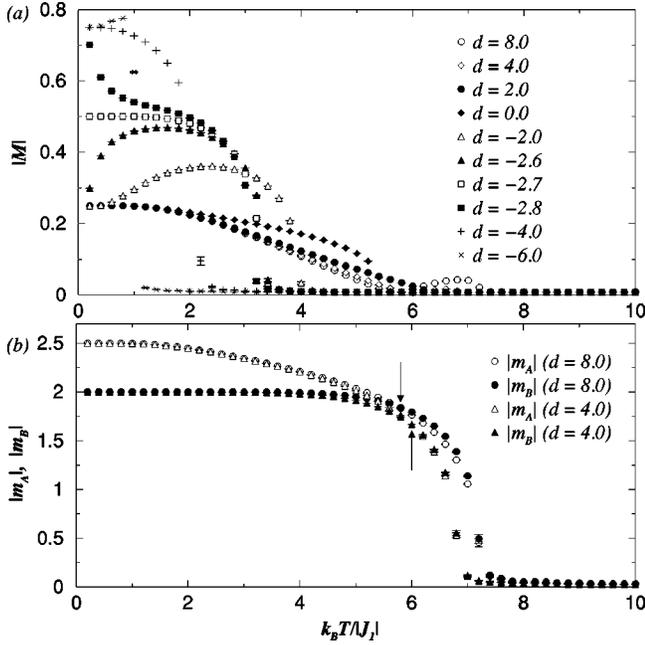
FIG. 4. Total and sublattice magnetization as a function of the temperature for several values of $D/|J_1|$ when $J_2/|J_1|$ is equal 0.2. Arrows in (b) represents the compensation points.

m_B only for $d=4.0$ and $d=8.0$ [Fig. 4(b)]. From this figure we can clearly recognize the existence of a compensation point for $d=4.0$ and 8.0 and a compensation point varies with the value of d. Arrows point the compensation temperatures. The result is in striking contrast with the one in the case of $j_2=0$. Without interlayer interactions, no compensation point was recognized even if a single-ion anisotropy constant is relatively large.[12,13] As for the type of magnetization curves, we can see four types of behavior. When d is equal to 4.0 or 8.0, the magnetization behaves as N-type curve in the Néel's classification[16] and behaves ferromagnetically (Q type) for $d=0.0$ and 2.0. In the case of $d=-2.0$ and -2.6, the magnetization curves become P type. $d=-2.7$ is the critical value since $j_2+d=-2.5$ is realized. The value of the total magnetization is 0.5, which indicates that the ground state is the state where spin-2 spins take a state $\sigma_j=1$ or $\sigma_j=2$ with equal probability and spin-$\frac{5}{2}$ spins take a state $S_i=-\frac{5}{2}$. The type of the magnetization curve is Q type. When d becomes just less than the critical value $d=-2.7$, the magnetization shows an interesting behavior. The magnetization curve falls rapidly from the maximum value $|M|=0.75$ at $T=0$, which is not predicted in the Néel's classification. As d becomes small further, the magnetization behaves Q and P type.

We can see from Fig. 4 that critical temperature (T_C) increases and compensation temperature (T_{comp}) (if it exists) decreased as d increases. In order to investigate the effects of d on the critical and compensation temperature, we draw a phase diagram in Fig. 5. T_C is approximately attained by locating the maxima of the specific heat curve shown in Fig. 6 and T_{comp} is the temperature where a total magnetization vanish below T_C. As shown in the phase diagram Fig. 5, T_C and T_{comp} seem to become insensitive to the change of d when d becomes large. Even when we carried out Monte Carlo simulations with the larger value of d, $d=20.0$, the
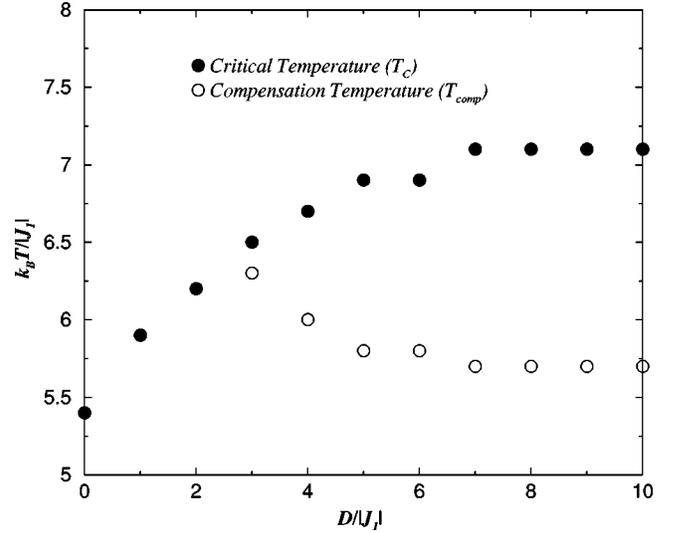

FIG. 5. The variations of the transition temperature T_C and the compensation temperature T_{comp} as a function of $D/|J_1|$ in the case of $J_2/|J_1|=0.2$.

values of T_C and T_{comp} are not effected. The compensation point can appear when d becomes larger than the critical value d_C which is estimated between 2.5 and 3.0 in the case of $j_2=0.2$. Note that the dip in T_C and the projection in T_{comp} near $d=6.0$ can be considered to be a statistical fluctuation.

B. Effects of interlayer interactions

Next, we fix the value of d to $d=0.0$ and vary j_2. Total and sublattice magnetization curves for several j_2 are shown in Fig. 7. In the case of $d=0.0$, the system is always in the $e_G=e_G^{(2)}$ region of the ground-state diagram (Fig. 2) for any $j_2(<0)$. Therefore the total magnetization at zero temperature is equal to 0.25 in absolute value. The variations of T_C and T_{comp} with the change of an interlayer interaction j_2 are depicted in Fig. 8. In the case of $j_2=0.0$, the system is equivalent to a two-dimensional honeycomb lattice system
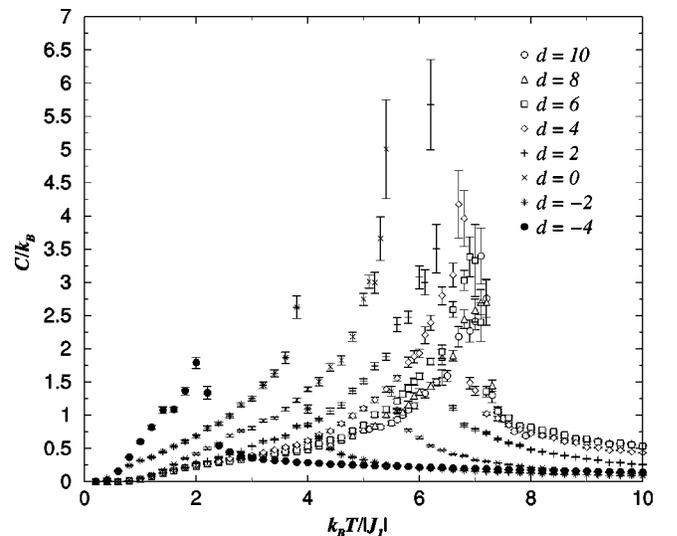

FIG. 6. Specific heats against k_BT/J for different values of $D/|J|$ in the case of $J_2/|J_1|=0.2$.
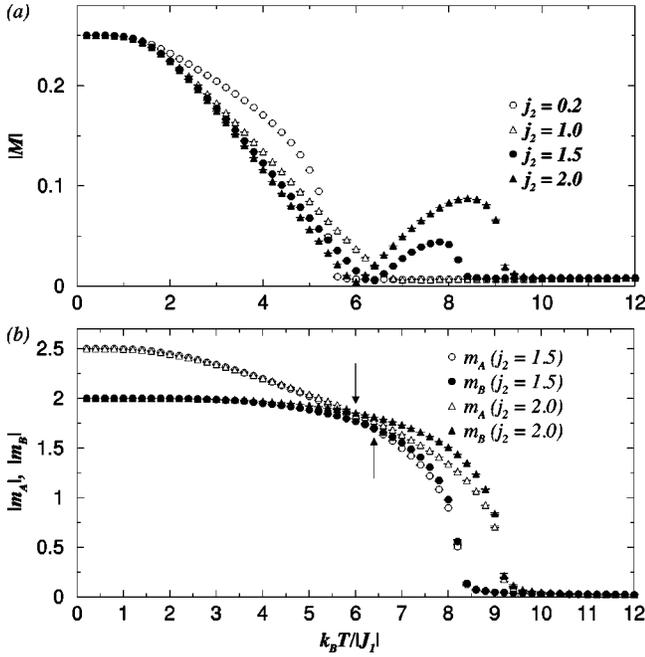
(a) *(b)*

FIG. 7. Total and sublattice magnetization as a function of the temperature for several values of $J_2/|J_1|$ in the case of $D/|J_1| = 0.0$. Arrows in (b) represents the compensation points.

and the critical temperature ($T_C \simeq 4.5$) for $j_2 = 0.0$ is equal to the result obtained for the two-dimensional system.[12,13] It is found from this figure that T_{comp} becomes insensitive to the change of j_2. T_C, however, keeps increasing with increase of the value of j_2.

Let us consider how the compensation phenomenon occurs. As j_2 increases, ferromagnetic interactions between $\sigma_j^{(l)}$ and $\sigma_j^{(l+1)}$ get stronger, which make it possible for spin-2 sublattice to remain ordered at higher temperatures. Furthermore if d is positive, the sublattice is easier to order. On the other hand, the spin-$\frac{5}{2}$ sublattice magnetization (m_A) decreases as temperature increases. Then, when j_2 is larger than a certain value, sublattice magnetization m_B exceeds m_A in magnitude at some temperature below the critical point.
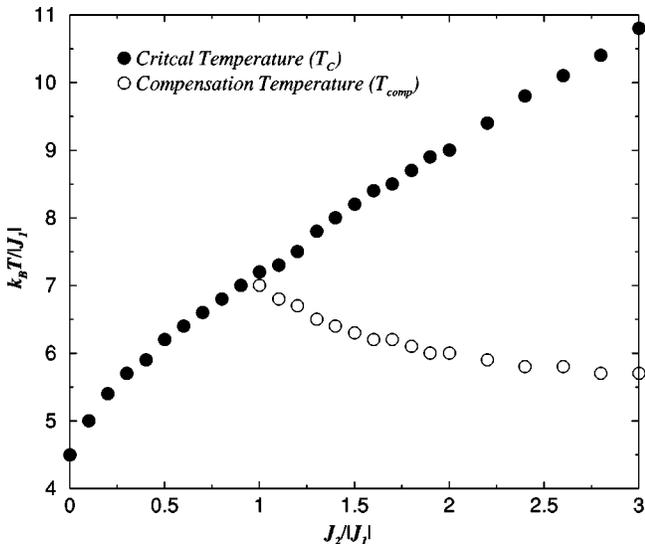

FIG. 8. Phase diagram of the system with $D/|J_1| = 0.0$ in the $T - J_2$ plane.
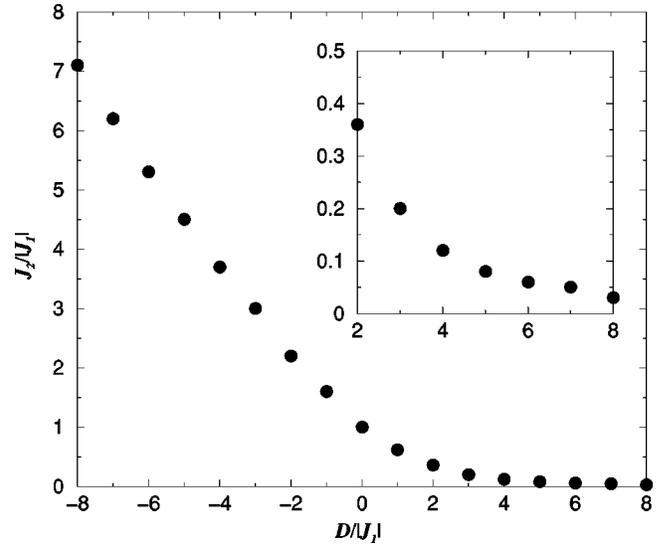

FIG. 9. Phase boundary above which the system shows a compensation phenomenon. In the inset we show the magnified figure for the range $2 \leqslant D/|J_1| \leqslant 8$.

It seems that interlayer interactions may play an important role for the existence of a compensation point. We calculate a minimum value of j_2, represented by j_2^{min}, above which a compensation point can appear for a certain value of d. Phase diagram, Fig. 9, shows the results. As d becomes large, j_2^{min} approaches to zero but will not reach zero, because there is no compensation point in the case of $j_2 = 0.0$. On the other hand, as d gets smaller, j_2^{min} becomes large linearly.

IV. CONCLUSION

We have applied Monte Carlo simulations to the study of a mixed spin-2 and spin-$\frac{5}{2}$ Ising model on a layered honeycomb lattice modeled by Eq. (1) in order to investigate a characteristic feature of $A\mathrm{Fe^{II}Fe^{III}(C_2O_4)_3}$ [$A = \mathrm{N}(n\text{-}C_nH_{2n+1})_4, n = 3\text{-}5$]. In particular, we have examined the effect of interlayer interactions and a single-ion anisotropy on the existence of the compensation point.

As is seen from Fig. 5, when there are interlayer interactions, there exists a critical value of d above which a compensation point can appear. This result contrasts sharply with that for the system without interlayer interactions.[12,13] On the other hand, even if d is equal to zero, a compensation point can be found when j_2 is larger than a certain value (see Fig. 8). These results suggest that including interlayer interactions is considered to be one of the cause for the compensation phenomenon. Our main result is summarized in Fig. 9. As d becomes large, j_2^{min}, above which a compensation point can appear, approaches to zero but does not reach zero. As d becomes small, j_2^{min} becomes large linearly.

Our results show that a compensation point appears when the interlayer interactions between spin-2 spins is included. Other studies for two-dimensional system suggest that the next-nearest-neighbors interaction is important for the existence of a compensation point.[8–10] Therefore it may be interesting to investigate effects of next-nearest-neighbors interactions between spin-2 spins in the same layer for our system. A compensation point may be possible even if j_2 is zero provided there are such longer-range interactions.

In this study we showed the results obtained form Monte Carlo simulations for the system with $N=L=20$. We also carried out simulations with larger system, say $N=L=40$, for several sets of parameters. We could not get much difference from the present results. Therefore our estimated values such as T_C, T_{comp}, and so on are considered to be reasonable. Needless to say, if we want precise thermodynamic values, we should perform finite-scaling analysis.

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