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Shun Tonooka[1]**, Koichi Kusakabe**[1]**, Naoshi Suzuki**[1] **and Hiroki Nakano**[2]

[1] Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama-cho, Toyonaka, Osaka 560-8531, Japan
[2] Graduate School and Faculty of Science, Himeji Institute of Technology, 3-2-1 Kouto, Kamigori-cho, Akou-gun, Hyougo 678-1297, Japan

Abstract

We investigate magnetic properties of the nanoscale ferrimagnetic ring $[Mn(hfac)_2NITPh]_6$ that is suggested to have a tendency of frustration. The spin densities of the candidate models are discussed. The spin density of the model with frustration shows characteristic behaviour different from those of the other models. Except for the quantum fluctuation which is a little bigger for the frustrated model, the difference in overall behaviour of the spin density is explained by the spin alignment in corresponding classical spin systems. The spin alignment is determined by competition of the Zeeman energy and the Mn–radical exchange interaction, when a canted spin alignment of Mn spins from the axis of the external magnetic field appears in the magnetization process for the other models, while it is absent for our frustrated model.

Recently, nanoscale molecular magnets have been extensively studied. One reason is that there is a possibility of realization of molecular devices by using these substances. Molecular magnets including radical spins are good candidates for the development of a new device because magnetic properties of the molecule may be easily optimized for the device with techniques such as chemical modification.

Among these molecular magnets, we focus on $[Mn(hfac)_2NITPh]_6$, abbreviated as Mn_6R_6, which was studied by several authors [1–4]. A molecule of this material contains six nitronyl nitroxide (NN) radical groups and six Mn ions. It is believed that there are an $S = 5/2$ local spin at each Mn site and an $S = 1/2$ local spin at each radical site. The spins at the Mn sites and those at the radical sites are coupled by an antiferromagnetic exchange forming the ring structure. Therefore, the $S^{tot} = 12$ ground state is realized. Kostyuchenko *et al* [2] measured the field derivative of the magnetization ($\chi(H)$) and reported four characteristic peaks. Based on the fitting of their experimental data with calculated results, they concluded that numerical data agree with the experimental data only when a three-spin interaction is taken into account
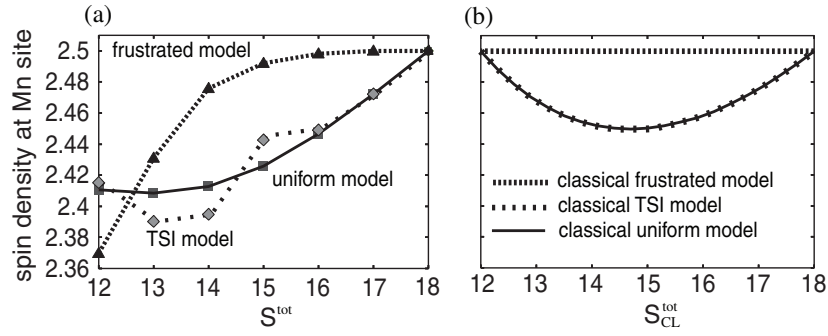
Figure 1. The spin density at a Mn site. The results in (a) are the results for the quantum spin systems. The results in (b) are the results for the corresponding classical spin systems.

in addition to the interaction between each Mn site and its nearest-neighbour (nn) radical sites. However, there remains an unresolved disagreement between the experimental data and the theoretical results that the number of experimentally observed peaks is inconsistent with the theoretical result.

In [4], the present authors investigated three candidate models which may reproduce the magnetization process of Mn_6R_6 by means of exact diagonalization based on the Lanczos algorithm. They fitted the experimental data [2] with the numerical results by a kind of the least squares method. An optimized set of interaction parameters were obtained for each model. The first one was a model considering only the nn Mn–radical Heisenberg interactions, which is called the uniform model, proposed by Caneschi *et al* [1]. The second one was a model considering the effect of three-spin interactions with the uniform model, which is called the three-spin interaction (TSI) model, proposed by Kostyuchenko *et al* [2]. The last one was a model considering the effect of next-nearest-neighbour (nnn) radical–radical antiferromagnetic interactions with the uniform model, which is called the frustrated model. The authors found that the frustrated model is the best one for reproducing the magnetization process of Mn_6R_6 well because the disagreement concerning of the number of peaks in $\chi(H)$ does not appear. They calculated the spin density at a Mn site from the state of $S^{tot} = 12$ to the one of $S^{tot} = 18$ in order to compare the ground-state wavefunctions of the uniform model, the TSI model and the frustrated model (results are shown in figure 1(a)). The spin density at a Mn site of the TSI model shows behaviour that is similar to that of the uniform model. The spin density of the uniform model decreases when $12 \leqslant S^{tot} \leqslant 13$ and then turns to increasing, showing a concave shape with further increasing S^{tot}. On the other hand, in the frustrated model, the spin density increases with S^{tot} convexly and rapidly saturates. The spin state of the frustrated model is considerably different from those of other cases. The purpose of this paper is to clarify the origin of this difference. For the purpose, we compare the case of the quantum and the corresponding classical spin systems.

Let us introduce the Hamiltonians. The spin systems are expressed by the following three Hamiltonians ($\mathcal{H}_0$, $\mathcal{H}_{3spin}$, $\mathcal{H}_{nnn}$):

$$\mathcal{H}_0 = \sum_{i=1}^{6} J_0 \mathbf{s}_{2i-1} \cdot \mathbf{S}_{2i} - g\mu_B h^z \sum_{i=1}^{6}(s_{2i-1}^z + S_{2i}^z) \tag{1}$$

$$\mathcal{H}_{3spin} = \mathcal{H}_0 + \mathcal{H}_3 - g\mu_B h^z \sum_{i=1}^{6}(s_{2i-1}^z + S_{2i}^z) \tag{2}$$

$$\mathcal{H}_3 = \sum_{i=1}^{6} J_3[(\mathbf{s}_{2i-1} \cdot \mathbf{S}_{2i})(\mathbf{S}_{2i} \cdot \mathbf{s}_{2i+1}) + (\mathbf{S}_{2i} \cdot \mathbf{s}_{2i+1})(\mathbf{s}_{2i-1} \cdot \mathbf{S}_{2i})] \tag{3}$$

$$\mathcal{H}_{\text{nnn}} = \mathcal{H}_0 + \sum_{i=1}^{6} J_2 \mathbf{s}_{2i-1} \cdot \mathbf{s}_{2i+1} - g\mu_{\text{B}} h^z \sum_{i=1}^{6} (s_{2i-1}^z + S_{2i}^z). \tag{4}$$

Here, $\mathbf{S}_{2i}$ and $\mathbf{s}_{2i-1}$ represent $S = 5/2$ and $1/2$ local spins, respectively. The periodic boundary condition $\mathbf{s}_1 = \mathbf{s}_{13}$ is imposed. The Zeeman term is considered as the effect of the external magnetic fields. We use $g = 2$. J_0 is the nn Mn–radical coupling constant. The optimized parameter of the uniform model is $J_0 = 24$ cm^{-1} in $\mathcal{H}_0$ [4]. J_3 is the coupling constant of the three-spin interaction. The optimized set of parameters of the TSI model is $J_0 = 40$ cm^{-1}, $J_3 = 6$ cm^{-1}, for $\mathcal{H}_{3\text{spin}}$ [4]. J_2 is the coupling constant of the nnn radical–radical interaction. The optimized set of parameters of the frustrated model is $J_0 = 42$ cm^{-1}, $J_2 = 90$ cm^{-1}, for $\mathcal{H}_{\text{nnn}}$ [4]. We also consider the corresponding spin systems composed of the classical vectors with the amplitudes $5/2$ and $1/2$ denoted by $\mathbf{S}_{\text{CL}2i}^{\text{Mn}}$ and $\mathbf{s}_{\text{CL}2i-1}^{\text{rad}}$, respectively. We calculate the z component of $\mathbf{S}_{\text{CL}2i}^{\text{Mn}}$ as a quantity corresponding to the spin density in the quantum spin systems. The total magnetization in the classical spin systems corresponds to S^{tot} in the quantum spin systems, which we denote as $S_{\text{CL}}^{\text{tot}}$. Note that S^{tot} and $S_{\text{CL}}^{\text{tot}}$ increase with the increase of the external magnetic fields.

The results for the classical spin systems are shown in figure 1(b). The behaviour of the spin density at a Mn site in the classical TSI model is the same as that in the classical uniform model. As $S_{\text{CL}}^{\text{tot}}$ increases, the spin density decreases when $12 \leqslant S_{\text{CL}}^{\text{tot}} \leqslant 14$ and increases when $15 \leqslant S_{\text{CL}}^{\text{tot}} \leqslant 18$. In the classical frustrated model, however, the spin density stays at 2.5 whenever $12 \leqslant S_{\text{CL}}^{\text{tot}} \leqslant 18$. This behaviour is distinguished from the behaviour in the non-frustrated models, i.e. the classical uniform model and the classical TSI model.

Let us discuss the behaviour of the spin density at a Mn site in the classical spin systems. In all the three cases, the Néel order is realized in the state $S_{\text{CL}}^{\text{tot}} = 12$ so that the spin density at a Mn site is 2.5 in this state. When the Néel order is realized, we suppose that $\mathbf{S}_{\text{CL}2i}^{\text{Mn}}$ is directed along the $+z$ axis and $\mathbf{s}_{\text{CL}2i-1}^{\text{rad}}$ is directed along the $-z$ axis because the direction of the magnetic fields is along the $+z$ axis. As $S_{\text{CL}}^{\text{tot}}$ increases in the classical uniform model and in the classical TSI model, $\mathbf{s}_{\text{CL}2i-1}^{\text{rad}}$ is rotated from the direction along the $-z$ axis by the Zeeman effect. $\mathbf{S}_{\text{CL}2i}^{\text{Mn}}$, on the other hand, is rotated from the $+z$ direction due to the J_0 interaction, although there is a loss of the Zeeman energy. That is, in the classical uniform model and in the classical TSI model, the effect of the J_0 interaction is larger than the Zeeman effect when $S_{\text{CL}}^{\text{tot}}$ increases from 12 to 14. As a result, the spin density at a Mn site decreases from the value at $S_{\text{CL}}^{\text{tot}} = 12$. In the classical frustrated model, however, $\mathbf{s}_{\text{CL}2i-1}^{\text{rad}}$ and $\mathbf{s}_{\text{CL}2i+1}^{\text{rad}}$ are inclined along the directions that are opposite to each other due to the J_2 interaction while the projection of a vector $\mathbf{s}_{\text{CL}2i-1}^{\text{rad}} + \mathbf{s}_{\text{CL}2i+1}^{\text{rad}}$ to the xy plane vanishes. Thus, the effect of the J_0 interaction on $\mathbf{S}_{\text{CL}2i}^{\text{Mn}}$ is partly cancelled. This causes the effect of the J_0 interaction to be smaller than the Zeeman effect in all the cases from $S_{\text{CL}}^{\text{tot}} = 12$ to 18. Consequently, the effect of the J_0 interaction does not work for the decrease of the spin density at a Mn site in the classical frustrated model. The spin density at a Mn site does not decrease in the classical frustrated model.

From this result, the difference in behaviour of the spin density at a Mn site in the quantum spin systems is understood. In the quantum spin systems, the spin density deviates from the one in the corresponding classical spin systems. Note here that the smaller S^{tot} is, the larger the quantum fluctuation is. In the uniform model and in the TSI model, the local spin density at the Mn site shows more or less a concave behaviour as a function of S_{tot}. Although the local spin density is decreased by the quantum fluctuation, this tendency can be understood via the properties found in the corresponding classical models mentioned above. On the other hand,

the origin of the deviation from 2.5 in the frustrated model is just the quantum fluctuation because the local density is constant in the corresponding classical model. In particular, the quantum effect is enhanced due to the frustration in comparison with the non-frustrated cases. As a result, the frustrated model shows the convex behaviour.

In summary, we have investigated the magnetic properties of Mn_6R_6, which should be considered as a kind of spin-frustrated system from the numerical calculation [4]. We have discussed the spin density at a Mn site by comparing the cases of the classical and the quantum spin systems. The origin of the difference in spin density between the frustrated model and the non-frustrated models has been clarified. In the non-frustrated models, the behaviour is essentially explained by the classical limit, where spins on Mn sites are canted by the competition between the Zeeman interaction and the Mn–radical exchange interactions. In the frustrated model, on the other hand, the behaviour of the spin density comes only from the quantum effect that is enhanced due to the frustration.

Acknowledgments

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