Collective magnetic excitation in a single-chain magnet by electron spin resonance measurements

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Collective magnetic excitation of the single-chain magnet (SCM) has been observed using high-frequency electron spin resonance (ESR). The observed ESR mode is attributed to the spin wave excitation with strong magnetic anisotropy where its temperature dependence shows the continuous evolution of the short-range spin correlation inside the chain. The uniaxial anisotropy constants and the exchange couplings of the related SCM have been quantitatively deduced from our theoretical analysis. Moreover, the relaxation mechanism of the SCM is found to originate from a collective reversal of spins via the transverse exchange couplings between the molecular units.

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I. INTRODUCTION

The synthesis of magnetic systems based on the molecular assembly is expected to be a gold mine of quantum phenomena due to its flexibility of controlling the dimensionality and its diversity of network. One example of these kinds of materials is the single-molecule magnet (SMM). The SMM, where the most well known compound is the Mn_{12}-ac, is an ensemble of identical molecular clusters in which the high-spin ground state is combined with the uniaxial anisotropy.[1] These clusters are well separated from each other, so that the intercluster exchange interactions are negligible. Hence, the magnetic system could be treated as a zero-dimensional system of an isolated cluster. Consequently, the system is well described by the discrete energy levels, and the quantum phenomena such as the tunneling can be observed.[1,2] Besides, recent developments in the coordination chemistry have made it possible to increase the dimensionality by connecting these SMMs, and create a variety of magnets from a one-dimensional (1D) to a three-dimensional (3D) system.[3–7] In particular, a quasi 1D system with strong uniaxial anisotropy and negligible interchain interactions is called single-chain magnet (SCM), and a variety of such SMM based 1D systems have been synthesized.[3–6]

For the past decades, the 1D magnetic system has attracted considerable interests, since the ideal 1D system shows no 3D long-range order and the quantum spin fluctuations lead to the appearance of some exotic quantum effects.[8–10] Although many intensive works have been done in the inorganic 1D system, many of those show long-range order due to the small interchain interactions unless the ground state is a singlet.[8,10–12] In contrast, the organic based SCM, where the 1D chains are stacked by van der Waals interactions or weak hydrogen bonding, is expected to be a better 1D system since the interchain couplings are infinitesimal.[3–6]

In general, the low energy excitation of the Heisenberg or Ising type ferromagnetic/ferrimagnetic chain is governed by the spin wave excitation or the spin cluster excitation, respectively. The spin wave excitation, where the spin wave propagates through the transverse exchange coupling of spins, is known as the elementary and collective magnetic excitation from the ground state in the ferromagnetic chain, while the spin cluster excitation is a localized magnetic excitation that is related to the flip of the spin, as schematically described in Fig. 1(a).[13–15]

Although the static and dynamic properties of the SCM have been recently well studied, the above-mentioned magnetic excitations have never been directly observed so far in the SCM.[16–19] Moreover, the interesting point to study the magnetic excitation of the SCM is that this system is in fact a finite chain system, which is synthesized from a series of SMM. Thus, the development of the spin reversal mechanism, from the resonant tunneling of the isolated SMM to the collective spin wave excitation in a chain, can be examined by varying the temperature. We stress that such spin reversal

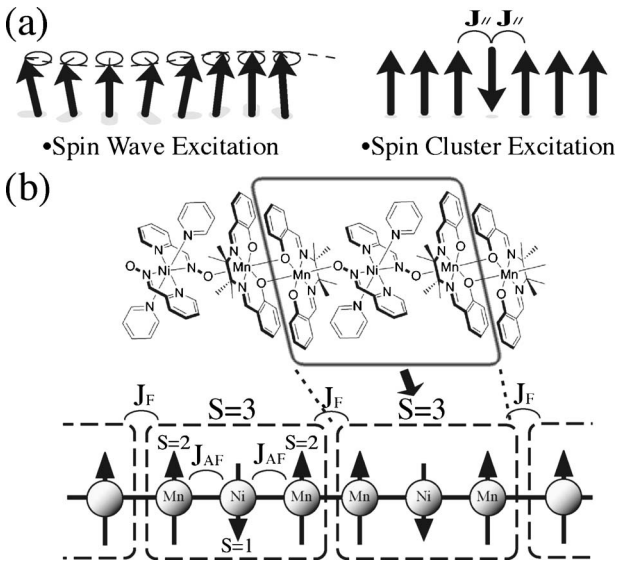

FIG. 1. (a) The schematic view of the spin wave excitation and the spin cluster excitation in the ferromagnetic chain. (b) The chain structure of $[Mn_2(saltmen)_2Ni(pao)_2(py)_2](ClO_4)_2$ and the schematic view of the [Mn(III)-Ni(II)-Mn(III)] trimer SCM.

TABLE I. Previous and present results of the magnetic properties of $[Mn_2(saltmen)_2Ni(pao)_2(py)_2](ClO_4)_2$. J_{AF} and J_F is the exchange couplings inside and between the trimer units. D_T is the effective anisotropy of the trimer unit. D_{Mn} and D_{Ni} is the local uniaxial anisotropy of the Mn(III) and Ni(II) ions, respectively. The units are in Kelvin.

	J_{AF}	J_F	D_T	D_{Mn}	D_{Ni}
Previous results[a],[b]	−21	+1.4	−2.5		
Present results	−18.6	+1.3		−5.1	0[c]

[a]Evaluated from the theoretical fitting of the macroscopic measurements (susceptibility and magnetization).
[b]See Refs. 4 and 5.
[c]$D_{Ni}=0$ is assumed in the fitting.

process is caused by the short-range spin correlation between SMM units in the SCM, and this appears as the temperature variation of the electron spin resonance (ESR) spectra. This is due to the special features of ESR that observe the magnetic mode in the long wavelength limit ($q=0$) and can pick up the short-range correlation very effectively.[20,21]

In this paper, we will report on the first observation of the collective magnetic excitation in the SCM, $[Mn_2(saltmen)_2Ni(pao)_2(py)_2](ClO_4)_2$, that has a ferromagnetic ground state. The paper is organized as follows. In Sec. II, we describe the basic properties of the studied SCM and our experimental methods. In Sec. III, we present the high-frequency ESR results and discuss about the origin of the observed ESR modes. In Sec. IV, we develop a theoretical model for the SCM, and the theoretical analysis of the observed results is presented. Finally, in Sec. V, we present conclusions with a brief summary.

II. BASIC PROPERTIES AND EXPERIMENT

The schematic views of the chain structure of the SCM, $[Mn_2(saltmen)_2Ni(pao)_2(py)_2](ClO_4)_2$, where saltmen=*N*, *N*-(1,1,2,2-tetramethylethylene) bis (salicylideneiminate); pao=pyridine-2-aldoximate; py =pyridine, are shown in Fig. 1(b). The aspects of this SCM are (i) the 1D chain consists of repeating units of antiferromagnetically (J_{AF}) coupled [Mn(III)-Ni(II)-Mn(III)] trimer ($S=3$), that is connected through a ferromagnetic interaction (J_F), (ii) the repeating trimer units have a strong uniaxial anisotropy, which is mainly due to the Mn(III) ions, and (iii) the interchain interaction is negligible due to the absence of interchain π overlaps between the organic ligands. Although this SCM does not show 3D magnetic ordering, the magnetization results show a ferromagnetic-like hysteresis behavior at low temperature.[4,5] By analyzing the temperature dependence of the magnetic susceptibility χ with the model of $S=3$ trimer chain, the exchange interactions inside and between the repeating trimer units have been quantitatively deduced as $J_{AF}=-21$ K and $J_F=1.4$ K, respectively.[4,5] Moreover, the uniaxial anisotropy has been obtained from the angular dependence of the magnetization.[5] The summary of these parameters is listed in Table I. It is also worth to noting that this

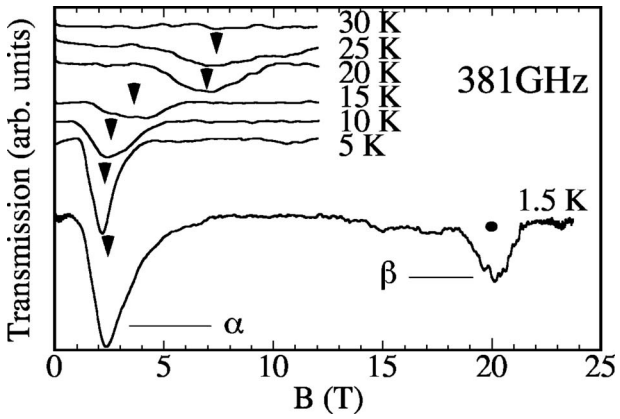

FIG. 2. The temperature dependence of the ESR spectra at 381 GHz. A powder sample was used for the study. The modes α and β are the modes for easy and hard axis, respectively.

SCM has a finite length due to the structural defects on the chain. The average length of the SCM, *L*, is estimated to be 90–110 trimer units from the saturation of χT.[16]

The high-field ESR measurements have been performed at the Tohoku University using pulsed magnetic field up to 25 T. The radiation was produced by Gunn oscillators, backward traveling wave oscillator (BWO), and an optically pumped far-infrared laser. We have employed a simple transmission method with the Faraday configuration. A powder sample was used for the study.

III. RESULTS AND DISCUSSIONS

Figure 2 shows the typical temperature dependence of the ESR spectra at 381 GHz. Two ESR modes, one at 2.4 T and the other at 20.2 T, were observed for 1.5 K, and we denote these as modes α and β, respectively. As it will be explained later, the modes α and β correspond to the mode for easy and hard axis, respectively. The mode α appears around 25 K and shifts drastically to lower field as the temperature decreases. In a 1D system, a distinct shift of the resonance field is generally observed when short-range correlation is developed.[20] The temperature range of the shift is in good agreement with the antiferromagnetic interaction of the SCM (i.e., $J_{AF}=-21$ K).[4,5] This fact strongly supports that the shift is due to the evolution of the short-range spin correlations inside the chain. In other words, the resonant tunneling spin reversal develops to a collective reversal mechanism by decreasing the temperature. We note that the mode β also shifts to lower field by increasing the temperature (not shown in the figure). Figure 3 shows the frequency dependence of the ESR spectra at 1.5 K. The resonance field of modes α and β increase linearly with the frequency. Although both modes α and β were observed for 357 and 381 GHz, only mode β was observed for 190 GHz. This suggests that there is a finite zero-field gap for mode α. The frequency-field diagram of modes α and β is presented in Fig. 4. Two parameters, the excitation gap $E_g=321$ GHz=15.4 K and $g=2$, are obtained from the linear extrapolation of mode α.

Next, let us discuss about the origin of these ESR modes. The schematic energy diagrams for Ising and Heisenberg chain, and SMM are shown in Fig. 5.

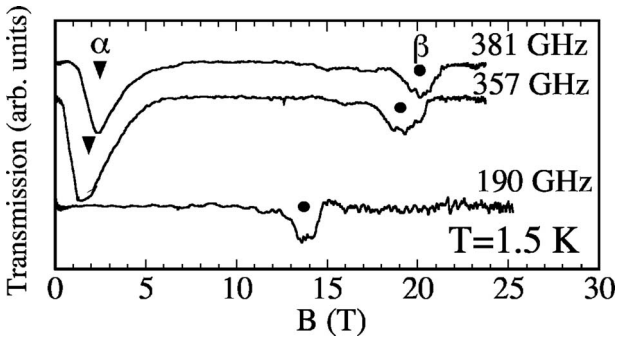

FIG. 3. The frequency dependence of the ESR spectra at 1.5 K. Both modes α and β were observed for 357 and 381 GHz, while only mode β was observed for 190 GHz.

For the Ising chain, two types of the ESR modes, the spin cluster excitation and the spin cluster resonance, are possible. The spin cluster excitation is corresponding to the flip of N-spin cluster from the ground state, while the spin cluster resonance corresponds to the single-spin flip between the excited states as shown in Fig. 5(a).[22] Hence, the spin cluster excitation is the transition of $\Delta S_z = \pm 2NS_u$ with an excitation gap of $2J_{\|}$, while the spin cluster resonance is a $\Delta S_z = \pm 2S_u$ transition without a gap at zero field. $J_{\|}$ represents the intrachain exchange interaction, and S_u is the total spin number of the cluster unit (i.e., $S_u = 3$ for the present SCM). The frequency-field diagram of mode α shows a finite gap in Fig. 4, which suggests the possibility of the spin cluster excitation. However, the spin cluster excitation should observe a series of ESR peaks, in which the slopes of the frequency-field diagram are $2gNS_u$, and such peaks were not observed. Therefore, we conclude that the observed modes are neither spin cluster excitation nor spin cluster resonance.

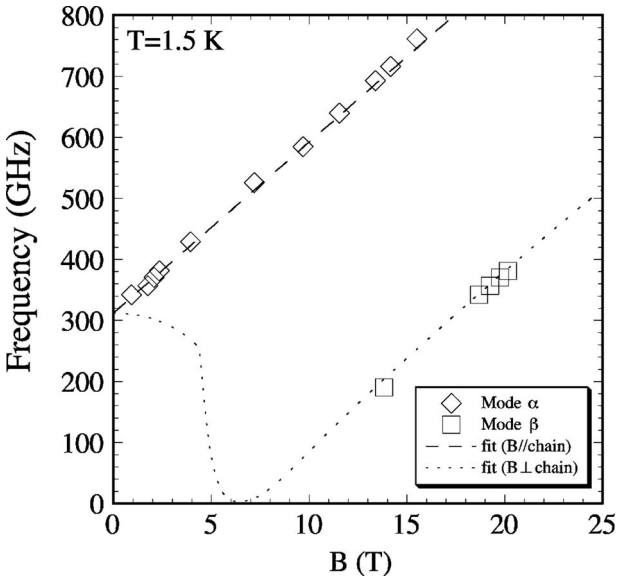

FIG. 4. The frequency-field diagram of the two observed modes. The diamond and square symbols represent the modes α and β, respectively. The broken and dotted lines are the theoretical calculation curves for $B\|$ chain and $B\perp$ chain, respectively. The calculation curves reproduce the experimental results when $J_{AF} = -18.6$ K, $J_F = +1.3$ K, $D_{Mn} = -5.1$ K, and $D_{Ni} = 0$ K.

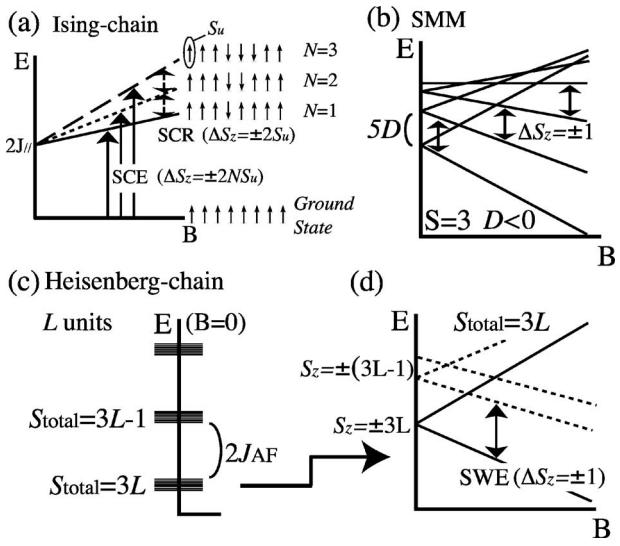

FIG. 5. The schematic energy diagrams of the (a) Ising chain, (b) SMM with $S=3$, (c) lowest part of the energy band in a finite Heisenberg chain with anisotropy at zero field, and (d) its energy diagram of $S_{total}=3L$ band. SCE, SCR, SMM, and SWE stand for spin cluster excitation, spin cluster resonance, single-molecule magnet, and spin wave excitation, respectively.

For the case of SMM, discrete absorptions, which are caused by the transitions in the multiplets with $\Delta S_z = \pm 1$, are usually observed [Fig. 5(b)]. The offset at zero field is related with the uniaxial anisotropy of the system. The intensity of the ESR mode for the SMM changes with the temperature, though the resonance field does not shift with the temperature. Therefore, the observed ESR modes are neither the SMM type transitions.

Then, let us consider for the case of a finite Heisenberg chain with an anisotropy. The zero-field energy diagram of an $S=3$ finite chain with L units is shown in Fig. 5(c). In that case, the lowest energy band is when all the spins in the units are aligned together, i.e., $S_{total}=3L$, and the next lowest band will be the $S_{total}=3L-1$ state, which costs approximately an energy of $2J_{AF}$ to the system. Therefore, only the transition within the multiplets of $S_{total}=3L$ band should be considered in our experiment at low temperature since J_{AF} is large as -21 K. This lowest band splits with the pairs of doublets, which is due to the uniaxial anisotropy constant D as partly shown in Fig. 5(d). At low temperature, the ground state is at the $S_z = \pm 3L$ state for $D<0$. Then, the possible ESR transition ($\Delta S_z = \pm 1$) is excitation from $S_z = -3L$ to $S_z = -(3L-1)$. It is to be noted that this excitation is referred to the spin wave excitation since this transition of S_z spread across the whole chain. In other words, the change of S_z is not caused by the local spin flip.

As mentioned above, the drastic shift in Fig. 2 is due to the short-range correlation inside the chain. Hence, this kind of behavior can be observed only in spin wave excitation, and a finite excitation gap is observed at zero field for spin wave excitation with significant uniaxial anisotropy. Therefore, the mode α can be attributed to the spin wave excitation with a strong magnetic anisotropy. The modes for easy and hard axis should be observed simultaneously since powder

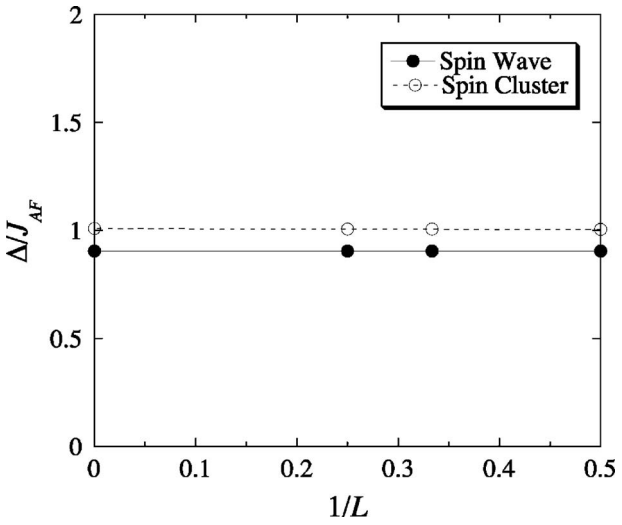

FIG. 6. System size dependence of the calculated excitation gaps for $J_{AF}=-18.6$ K and $J_F=1.3$ K, and $D_{Mn}=-5.1$ K. The solid and open circle correspond to the spin wave and spin cluster excitations, respectively. It suggests that the size corrections are quite small for all the excitation gaps.

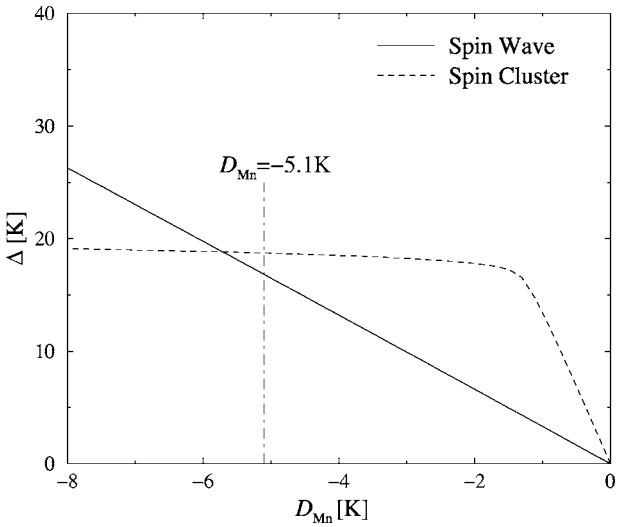

FIG. 7. The anisotropy dependence of the spin wave (solid curve) and cluster (dashed curve) excitation gaps of the four-unit system calculated by the Lanczos algorithm for $J_{AF}=-18.6$ K and $J_F=1.3$ K. It is found that the two excitation energies are very close to each other at the most suitable value $D_{Mn}=-5.1$ K for the present sample.

samples were used for this study. Hence, the modes α and β are the easy-axis and hard-axis modes for spin wave excitation, respectively.

IV. THEORETICAL ANALYSIS

Next, let us develop a theoretical model and analyze quantitatively our ESR results. The excitation gap (i.e., transition energy of ESR) has been calculated by using the following Hamiltonian,

$$\mathcal{H} = J_{AF}\sum_{i=1}^{L}[\mathbf{S}_{3i-2}\cdot\mathbf{s}_{3i-1}+\mathbf{s}_{3i-1}\cdot\mathbf{S}_{3i}] + J_F\sum_{i=1}^{L}[\mathbf{S}_{3i}\cdot\mathbf{S}_{3i+1}] + D_{Mn}\sum_{i=1}^{L}[S_{z,3i-2}^2+S_{z,3i}^2] + D_{Ni}\sum_{i=1}^{L}[s_{z,3i-1}^2] + \mathcal{H}_{Zeeman}. \quad (1)$$

The first and the second term are the intratrimer and intertrimer exchange couplings, respectively. $\mathbf{S}=2$ and $\mathbf{s}=1$ were used in the Hamiltonian. The third and the fourth term are the terms for the anisotropic constants inside the trimer units. Using the numerical exact diagonalization based on the Lanczos algorithm, we calculated the lowest energy eigenvalue in each subspace specified by ΣS_z and the wave vector k under the periodic boundary condition. In this model, the lowest-energy state is at $k=0$ for every value of ΣS_z.

Figure 6 shows the calculated excitation gaps of the spin wave ($\Delta S_z=-1$) and spin cluster ($\Delta S_z=-6$) excitations for $L=2,3,4$ units and the estimated values in the thermodynamic limit (i.e., $1/L=0$). The parameters were fixed to the most suitable ones obtained below.

We found that the energy converges sufficiently with a model of three units, which suggests the size effect is tiny. Hence, we have adopted the model of four units to fit the ESR modes of Fig. 4. Moreover, the anisotropy of Ni(II), D_{Ni}, has been neglected since the anisotropy of Mn(III), D_{Mn}, is large and D_{Ni} does not affect the results. We note that the axis of the uniaxial anisotropy is along the chain axis from the structure.

The best fit curves for $B\|$ chain and $B\perp$ chain are shown in Fig. 4. The theoretical curves reproduce well our ESR results when $J_{AF}=-18.(6)$ K, $J_F=+1.(3)$ K, $D_{Mn}=-5.(1)$ K, and $D_{Ni}=0$ K, and these values are in good agreement with the previous results obtained from the susceptibility and magnetization measurements (see Table I). The errors of the parameters J_{AF} and D_{Mn} are within a few percent, but 15% in J_F.

The D_{Mn} dependence of the spin wave and cluster excitation gaps, calculated with the values of J_{AF} and J_F obtained above, are shown in Fig. 7. It suggests that, by increasing the anisotropy $|D_{Mn}|$, the lowest excitation changes from the spin wave to the cluster excitations at a cross over point of $D_{Mn}\sim-5.7$ K. In the present sample ($D_{Mn}=-5.1$ K), the cluster excitation is revealed to be close to the spin wave excitation. However, the cluster excitation cannot be observed in any ESR measurements, because it is a very higher-order spin flip process. More precise theoretical study on the dynamical behavior of the SCM can be found elsewhere.[23]

V. CONCLUSIONS

In conclusion, we have reported on the observation of the collective magnetic excitation in the SCM. The observed magnetic excitation is attributed to the spin wave excitation with strong anisotropy from the frequency and temperature dependence of the ESR.

The observation of the spin wave excitation shows clearly that a spin reversal in a finite chain of SCM is caused by the

collective excitation due to the spin-spin correlation. It is interesting to find that such collective excitation is already the dominant mechanism for spin reversal at the chain length of 100. We believe that this is an important contribution for finite but large molecular magnets synthesized by supermolecular approach. We note that a collective propagation of a local charge by correlation is a similar but also a fundamental problem investigated intensively in other fields such as the photoinduced phase transition.[24]

Moreover, microscopic characterizations, such as the determination of the uniaxial anisotropy constants and the exchange couplings, have been done from the theoretical analysis of our ESR results. We have also calculated the condition of D in the SCM for behaving like the Ising model (i.e., spin cluster excitation becomes dominant).[23] The spin cluster excitation and the spin wave excitation are almost degenerated in our system, and the spin cluster excitation is slightly above spin wave excitation. Hence, the reason of not observing the spin cluster excitation is interesting, and this explanation could be related to the selection rule of ESR that favors the observation of spin wave excitation.

Next, let us comment briefly on the relation of the slow relaxation observed in the ac susceptibility to our results.[4,5,16] If the temperature is above the energy gap of spin wave excitation, the relaxation is dominated by spin wave excitation. Then, the relaxation should decay with the excitation gap at low temperature. In other words, the slow relaxation is due to the collective reversal of spins in the finite chain. However, related topics such as the source of the spin reversal, or the temperature dependence of the dominant excitation (spin wave excitation or spin cluster excitation) and its relaxation mechanism, remain as the future issues.

Finally, this work has shown that the high-frequency ESR is the effective and powerful technique to observe the magnetic excitation in the SCM systems. Examination of the dispersion of the excitation in the SCM by neutron scattering is a challenging subject for the future.

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