Modified spin-wave description of the nuclear spin relaxation in ferrimagnetic Heisenberg chains

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We make a modified spin-wave description of the nuclear spin relaxation in Heisenberg alternating-spin chains with antiferromagnetic exchange coupling. In contrast with the conventional one-dimensional antiferromagnetic spin-wave theory, which is plagued with the divergence of the sublattice magnetization even in the ground state, the present spin-wave description is highly successful over a wide temperature range. The temperature dependence of the relaxation rate $T_1^{-1}$ significantly varies with the crystal lattice structure, exhibiting both ferromagnetic and antiferromagnetic aspects. $T_1^{-1}$ further shows a unique dependence on the applied field, which turns out an indirect observation of the quadratic dispersion relations.

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I. INTRODUCTION

Quantum mixed-spin chains with magnetic ground states, namely, quantum ferrimagnets, are one of the hot topics and recent progress [1–25] in the theoretical understanding of them deserves special mention. Coexistent ferromagnetic and antiferromagnetic long-range orders [2] in the ferrimagnetic ground state in particular interest us. The ground-state magnetizations of antiferromagnets and ferrimagnets are zero and saturated, respectively, and therefore ferrimagnets may be recognized to possess in-between ground states. Hence the ground-state excitations in ferrimagnets are twofold [1–4]. The elementary excitations of ferromagnetic aspect, reducing the ground-state magnetization, form a gapless dispersion relation, while those of antiferromagnetic aspect, enhancing the ground-state magnetization, are gapped from the ground state. The dual structure of the excitations results in unique thermal behaviors [4, 6, 8, 2–24]: The specific heat and the magnetic susceptibility times temperature exhibit peculiar to quantum ferrimagnets. In response to these interesting aspects of quantum ferrimagnets. To the best of our knowledge, in the theoretical field, it was not until quite recently that the dynamic structure factors were calculated [11], while in the experimental field, any direct observation of the energy structure is not yet so successful, for instance, as that [36] for the Haldane antiferromagnets. In such circumstances, Fujiwara and Hagihara performed [39] nuclear-magnetic-resonance (NMR) measurements on bimetallic chain compounds. The measured temperature and applied-field ranges were rather limited and their argument was not so conclusive. However, they suggested that the nuclear spin relaxation could be a useful tool in order to look into the low-energy structure peculiar to quantum ferrimagnets. In response to this stimulative experiment, here we calculate the nuclear spin relaxation rate $T_1^{-1}$ in terms of a modified spin-wave theory and strongly encourage further experimental investigations.

Gleizes and Verdaguer and stimulated the public interest in this potential subject. The following examples [29–30] of an ordered bimetallic chain, MnCu(pba)(H$_2$O)$_3$$\cdot$2H$_2$O (pba = 1,3-propylenebis(oxamato) = C$_7$H$_6$N$_2$O$_6$) and MnCu(pbaOH)(H$_2$O)$_3$ (pbaOH = 2-hydroxy-1,3-propylenebis(oxamato) = C$_7$H$_6$N$_2$O$_7$), exhibiting more pronounced one dimensionality, activated further physical [11–13], as well as chemical [24], investigations. The serial chemical explorations condensed into the crystal engineering of a molecule-based ferromagnet [33] — the assembly of the highly magnetic molecular entities within the crystal lattice in a ferromagnetic fashion.

Thus, a good amount of chemical knowledge on quasi-one-dimensional quantum ferrimagnets has been accumulated and static properties of them have been revealed well. However, little is known about dynamic properties of quantum ferrimagnets. To the best of our knowledge, in the theoretical field, it was not until quite recently that the dynamic structure factors were calculated [11], while in the experimental field, any direct observation of the energy structure is not so successful, for instance, as that [36] for the Haldane antiferromagnets. In such circumstances, Fujiwara and Hagihara performed [39] nuclear-magnetic-resonance (NMR) measurements on bimetallic chain compounds. The measured temperature and applied-field ranges were rather limited and their argument was not so conclusive. However, they suggested that the nuclear spin relaxation could be a useful tool in order to look into the low-energy structure peculiar to quantum ferrimagnets. In response to this stimulative experiment, here we calculate the nuclear spin relaxation rate $T_1^{-1}$ in terms of a modified spin-wave theory and strongly encourage further experimental investigations.

II. FORMULATION

We describe alternating-spin chain compounds by the Hamiltonian
\[ \mathcal{H} = J \sum_{j=1}^{N} (\mathbf{S}_j \cdot \mathbf{s}_j + \mathbf{s}_j \cdot \mathbf{S}_{j+1}) - g\mu_B H \sum_{j=1}^{N} (S_j^z + s_j^z), \]

(2.1)

where \( S_j^z = S(S + 1), \ s_j^z = s(s + 1) \), and we have set their \( g \) factors both equal to \( g \) because the difference between them amounts to at most several percent of themselves in practice [40]. We further set the unit-cell length, which is twice the lattice constant, equal to unity in the following for the convenience of calculation. Magnetic properties of the ferrimagnetic family compounds such as MCu(pba)(H2O)3-2H2O and MCu(pbaOH)(H2O)3 (M = Mn, Ni) are well described within this isotropic Hamiltonian [29,30,40,41]. Considering the electronic-nuclear energy-conservation requirement, the direct (single-magnon) process is of little significance but the Raman (two-magnon) process plays a leading role in the nuclear spin-lattice relaxation [42]. Then the relaxation rate is generally given by

\[
\frac{1}{T_1} = \frac{4\pi(g\mu_Bh\gamma_N)^2}{\hbar} \sum_{n,m} e^{-E_n/\hbar k_BT} \times |\langle m | (A_j^z S_j^z + a_j^z s_j^z) | n \rangle|^2 \delta(E_m - E_n - \hbar\omega_N), \tag{2.2}
\]

where \( A_j^z \) and \( a_j^z \) are the dipolar coupling constants between the nuclear and electronic spins in the \( j \)-th unit cell, \( \omega_N = \gamma_N H \) is the Larmor frequency of the nuclei with \( \gamma_N \) being the gyromagnetic ratio, and the summation \( \sum_n \) is taken over all the electronic eigenstates \( |n\rangle \) with energy \( E_n \).

In order to rewrite the Hamiltonian [2,3] within the framework of the spin wave theory, we introduce the bosonic operators for the spin deviation in each sublattice via

\[
S_j^+ = \sqrt{2S - a_j^z a_j}, \quad S_j^- = S - a_j^z a_j, \quad S_j^z = s = b_j^z b_j, \quad S_j^z = -s + b_j^z b_j, \tag{2.3}
\]

where we regard \( S \) and \( s \) as quantities of the same order.

Now we obtain the bosonic Hamiltonian as

\[ \mathcal{H}_{SW} = E_{\text{class}} + \mathcal{H}_0 + \mathcal{H}_1 + O(S^{-1}), \tag{2.4} \]

where \( E_{\text{class}} = -2sSJN \) is the classical ground-state energy, and \( \mathcal{H}_0 \) and \( \mathcal{H}_1 \) are the one-body and two-body terms of the order \( O(S^1) \) and \( O(S^0) \), respectively. We may consider the simultaneous diagonalization of \( \mathcal{H}_0 \) and \( \mathcal{H}_1 \) in the naivest attempt to go beyond the linear spin-wave theory. However, such an idea ends in failure bringing a gap to the lowest-lying ferromagnetic excitation branch. Thus we take an alternative approach [13] at the idea of first diagonalizing \( \mathcal{H}_0 \) and next extracting relevant corrections from \( \mathcal{H}_1 \). \( \mathcal{H}_0 \) is diagonalized as

\[ \mathcal{H}_0 = E_0 + \sum_k (\omega_k^+ \alpha_k + \omega_k^- \beta_k^\dagger), \tag{2.5} \]

where \( E_0 = \sum_k [\omega_k(S + s)] \) is the \( O(S^1) \) quantum correction to the ground-state energy, and \( \alpha_k \) and \( \beta_k \) are the creation operators of the ferromagnetic and antiferromagnetic spin waves of momentum \( k \) whose dispersion relations are given by

\[
\omega_k^\pm = \omega_k \pm (S - s)J \mp g\mu_B H, \tag{2.6}
\]

with

\[
\omega_k = J\sqrt{(S - s)^2 + 4S^2 sin^2(k/2)}. \tag{2.7}
\]

**FIG. 1.** Dispersion relations of the ferromagnetic and antiferromagnetic elementary excitations, namely, the lowest-energy states in the subspaces of \( M = N/2 \mp 1 \). The linear- and interacting-spin-wave calculations are shown by the dotted and solid lines, respectively, whereas \( \times \) represents the quantum Monte Carlo estimates (\( N = 32 \)). Here we plot the excitation energy \( E(k) \) taking the ground-state energy as zero.
The Wick theorem allows us to rewrite $H_1$ as

$$\mathcal{H}_1 = E_1 - \sum_{k} \left( \delta\omega_k \kappa_1^\dagger \kappa_k + \delta\omega_k \beta_1^\dagger \beta_k \right) + \mathcal{H}_{\text{irrel}} + \mathcal{H}_{\text{quart}},$$

where $\mathcal{H}_{\text{irrel}}$ contains irrelevant terms such as $\alpha_k \beta_k$ and $\mathcal{H}_{\text{quart}}$ contains residual two-body interactions, both of which are neglected in the following so as to keep the low-energy structure qualitatively unchanged. $E_1 = -2JN[I_1^2 + I_2^2 + (\sqrt{S}/s + \sqrt{s}/S)I_1I_2]$ is the $O(S^0)$ correction to the ground-state energy, while

$$\delta\omega_k^\pm = 2(S + s)I_1 \frac{\sin^2(\kappa(k/2))}{\omega_k} + \frac{I_2}{\sqrt{SS}} [\omega_k \pm (S - s)],$$

are those to the dispersions, where the key constants $I_1$ and $I_2$ are defined as $I_1 = (2N)^{-1} \sum_k ((S + s)/\omega_k - 1)$ and $I_2 = -N^{-1} \sum_k (\sqrt{S}/\omega_k) \cos^2(k/2)$. The resultant Hamiltonian is compactly represented as

$$\mathcal{H}_{\text{SW}} \simeq E_0 + \sum_k \left( \omega_k \kappa_1^\dagger \kappa_k + \omega_k \beta_1^\dagger \beta_k \right),$$

with $E_0 = E_{\text{class}} + E_0 + E_1$ and $\omega_k^\pm = \omega_k^\pm - \delta\omega_k^\pm$.

We show in Fig. 1 the linear- and interacting-spin-wave dispersions, $\omega_k^\pm$ and $\omega_k^\pm$, together with the numerical solutions [24] obtained through imaginary-time quantum Monte Carlo calculations [43, 45]. The spin-wave description of the low-energy structure is fairly good. Even the linear spin waves allow us to have a qualitative view of the elementary excitations. The relatively poor description of the antiferromagnetic branch by the linear spin waves reminds us of the spin-wave treatment of monospin Heisenberg chains, where the theory accurately describes ferromagnetic chains, while it only gives a qualitative view of antiferromagnetic chains. The spin-wave approach to the present system is highly successful anyway for both excitation branches. The spin-wave series potentially lead to the goal even for the antiferromagnetic branch. The high applicability essentially originates in the fact that the spin deviations

$$\frac{1}{N} \sum_j (a_j^\dagger a_j) = \frac{1}{N} \sum_j (b_j^\dagger b_j) = \Gamma_1$$

$$= \frac{1}{2\pi} \int_0^\pi \left[ \frac{S + s}{\sqrt{(S - s)^2 + 4Ss \sin^2(k/2)}} - 1 \right] dk,$$

with $\langle \cdot \rangle$ denoting the ground-state average, no more diverge in the present system with $S \neq s$. We are convinced that the quantity $\Gamma_1$ should be recognized as the quantum spin reduction.

In terms of the spin waves, the relaxation rate (2.2) is expressed as

$$\frac{1}{T_1} = \frac{4\pi \hbar}{N^2} (g\mu_B \gamma N)^2 \sum_{k,q} \sum_{\sigma = \pm} \delta(\omega_k^+ + \omega_k^- - \hbar \omega_N) \times \left[ (A_k^+ \cos \theta_k \sigma_k^+ + A_k^- \cos \theta_k \sigma_k^-)^2 n_k^\sigma (n_k^\sigma + 1) + (A_k^+ \sin \theta_k \sigma_k^+ + A_k^- \sin \theta_k \sigma_k^-)^2 n_k^\sigma (n_k^\sigma + 1) - 2A_k^+ A_k^- (\cos \theta_k \sigma_k^+ \cos \theta_k \sigma_k^-)^2 n_k^\sigma (n_k^\sigma + 1) \right],$$

where $n_k^\pm = \langle \alpha_k^\dagger \alpha_k \rangle$ and $n_k^\pm = \langle \beta_k^\dagger \beta_k \rangle$ are the thermal averages of the boson numbers at a given temperature, and $A_k^\pm = \sum_j e^{i\omega j - \beta_j / A_k^\pm}$ and $a_k^\pm = \sum_j e^{i\omega j + 1 / 4} a_j^\pm$ are the Fourier components of the hyperfine coupling constants. Taking into account the significant difference between the electronic and nuclear energy scales ($\hbar \omega_N \lesssim 10^{-5} J$), Eq. (2.12) ends in

$$\frac{1}{T_1} = \frac{4\hbar}{N^2} (g\mu_B \gamma N)^2 \sum_k \frac{S - s}{\sqrt{(Ssk)^2 + 2(S - s)S^2 s^2 / s}} \times \left[ (A_k^+ \cos^2 \theta_k - a_k^\sigma \sin^2 \theta_k)^2 n_k^\sigma (n_k^\sigma + 1) + (A_k^\sigma \sin^2 \theta_k - a_k^\sigma \cos^2 \theta_k)^2 n_k^\sigma (n_k^\sigma + 1) \right],$$

where we have assumed little $k$-dependence of $A_k^\sigma$ and $a_k^\sigma$, and thus replaced $A_k^\sigma = -2k$ and $a_k^\sigma = 2k$ by $A_k^\sigma = 0 \equiv A^\sigma$ and $a_k^\sigma = 0 \equiv a^\sigma$, respectively.

The estimation of the relaxation rate is now reduced to the calculation of the spin-wave distribution functions. Though the ground-state distribution is well controlled, the naivest thermodynamics, based on the partition function $Z = Tr[e^{-H_{\text{SW}} / k_B T}]$, breaks down as temperature increases. Hence we modify the spin-wave theory [46, 49] introducing an additional constraint in minimizing the free energy. Requiring the total magnetization to be zero, Takahashi [46] obtained an excellent description of the low-temperature thermodynamics of one-dimensional Heisenberg ferromagnets. Taking his core idea but replacing the ferromagnetic constraint $\sum_j (S_j^z + s_j) = 0$ by

$$\sum_j (S_j^z - s_j^\sigma) + 2\Gamma_1 = (S + s) \left( N - \sum_k \sum_{\sigma = \pm} \frac{n_k^\sigma}{\omega_k} \right) = 0,$$

we obtain the modified spin-wave distribution functions as

$$n_k^\pm = \frac{1}{e^{[\omega_k^\pm - \mu(S + s)] / k_B T} - 1},$$

with a Lagrange multiplier $\mu$ due to the condition (2.14). In comparison with the ferromagnetic cases, the quantum correction $2\Gamma_1$ is necessary for ferrimagnets. The spin-wave treatment gives $\langle S_j^z + s_j \rangle = S + s$ under ferromagnetic exchange coupling but $\langle S_j^z - s_j \rangle = S + s - 2\Gamma_1$ under antiferromagnetic exchange coupling. Indeed, without the quantum correction, we reach a quite poor description of the thermal quantities [12]. We show in Fig.
the modified spin-wave calculations of the magnetic-susceptibility-temperature product, which is closely related with the relaxation rate and is given in terms of $n_k^\sigma$ as

$$\chi T = \frac{(g\mu_B)^2}{3k_B} \sum_k \sum_{\sigma = \pm} n_k^\sigma (n_k^\sigma + 1).$$  \tag{2.16}$$

The obtained results are fairly successful considering that these are the spin-wave calculations in one dimension. The modified spin waves well reproduce the low-temperature ferromagnetic divergence, which is proportional to $T^{-1}$, the high-temperature antiferromagnetic increase toward the paramagnetic behavior $[S(S + 1) + s(s+1)]/3$, and therefore, the round minimum at intermediate temperatures. In particular, the low-temperature description by the interacting spin waves may be regarded as accurate. Now we proceed to the argument of the relaxation rate in terms of the modified interacting-spin-wave theory. Since the applied field $H$ is so small in practice as to satisfy $g\mu_B H \lesssim 10^{-2}J$, we neglect the Zeeman term of the Hamiltonian (2.10) in the estimation of $n_k^\pm$.

III. RESULTS

Here still remains an adjustable parameter $A^2/a^2 \equiv r$. The dipolar coupling is quite sensitive to the location of the nuclei because the coupling strength is proportional to $d^{-3}$ with $d$ being the distance between the interacting nuclear and electronic spins. In the proton-NMR measurements on NiCu(pba)(H$_2$O)$_3$·2H$_2$O [33], for instance, it was demonstrated that the protons relevant to the relaxation rate do not originate in the H$_2$O molecules but lie in the pba groups which are located beside the Cu ions. Thus, for these family compounds, $r$ may reasonably be set equal to zero. We show in Fig. 3 the corresponding calculations. As the measurements were performed at rather high temperatures, which are beyond the quantitative reliability of the present theory, it is impossible to fit the calculations to the experimental findings. However, the calculations at $r = 0$ well explain the observations of monotonically decreasing behaviors of $T^{-1}$ as a function of temperature, which are in contrast with the appearance of $\chi T$. When we compare Eqs. (2.13) and (2.16), we
realize that $T_1^{-1}$ could tell more than $\chi T$ due to its adjustable prefactors to $n^2_k(n^2_k + 1)$. Setting $r$ equal to 0.4, we obtain temperature dependences of $T_1^{-1}$ exhibiting a round minimum, where the antiferromagnetic spin-wave contribution $n_k^-$ is much more accentuated than the ferromagnetic one $n_k^+$. Let us observe the momentum dependences of $n_k^\pm$ in Fig. 4. $n^-_k$ exhibits a sharp peak around $k = 0$ at low temperatures, which is rapidly reduced with the increase of temperature. On the other hand, $n^+_k$ is an increasing function of temperature at an arbitrary momentum, though its broad peak is smeared out with the increase of temperature. The field-dependent prefactor in Eq. 2.13, coming from the energy conservation requirement $\delta(E_m - E_n - \hbar \omega N)$ in Eq. 2.2, predominantly extracts the $k = 0$ components from $n^\pm_k$. Therefore, the parametrization $r = 0.4 \simeq \frac{1}{2} = \tanh^2 \theta_{k=0}$ results in the strong suppression of the ferromagnetic aspect of $T_1^{-1}$.

Another motivation of the NMR measurements on ferrimagnetic chains may be the characteristic field dependences of $T_1^{-1}$ shown in Fig. 3. It is due to the quadratic dispersion relations (2.6) that $T_1^{-1}$ depends on the applied field. Hence the present field dependence allows us to look into the low-energy structure peculiar to ferrimagnets. The high linearity of $T_1^{-1}$ with respect to $H^{-1/2}$ denotes the predominance of the $k \simeq 0$ compo-
ments in the $k$-summation in Eq. (2.13). The predominance is reduced with the increase of $H$ and finally there arises a logarithmic field dependence of $T^{-1}_f$ from the $k$-integration of $[(Sk)^2 + 2(S - s)Sh_{SN}]/J^{-1}/2$. If we take $J/k_B = 121$[K], $^1'H$ relevant to NiCu(pba)(H$_2$O)$_3$·2H$_2$O, Fig. 3 suggests that the logarithmic behavior should appear under $H \gtrsim 10$[T]. The $T_1$ measurements [43] on NiCu(pba)(H$_2$O)$_3$·2H$_2$O at 280[K] with an applied field up to 3.15[T] resulted in a monotonic linear dependence of $T^{-1}_f$ on $H^{-1}/2$. The high-field measurements at lower temperatures are expected.

In order to stimulate extensive NMR measurements on ferrimagnetic compounds, we show in Fig. 3 the temperature dependences of $T^{-1}_f$ in general constituent-spin cases. We select three particular values of $r$: (a) $r = 0$, where the relevant nuclei are located closer to the smaller spins $s$ and the ferromagnetic and antiferromagnetic mixed nature is displayed; (b) $r = \tanh^2\theta k_{eq}=0$, where the relevant nuclei are located near the smaller spins $s$ rather than the larger spins $S$ and the ferromagnetic aspect is strongly suppressed; and (c) $r = \cosh^2\theta k_{eq}=0$, where the relevant nuclei are located near the larger spins $S$ rather than the smaller spins $s$ and the antiferromagnetic aspect is strongly suppressed. Thus, the chemical technique might enable us to extract separately the ferromagnetic/antiferromagnetic feature of ferrimagnets from $T^{-1}_f$. Let us observe the temperature dependences from the point of view of the low-energy structure, which has been revealed in Fig. 1. The distinct behaviors shown in Fig. 3(b) and Fig. 3(c) are reminiscent of the antiferromagnetic and ferromagnetic $\chi T$ products, respectively. The antiferromagnetic aspect should be dominated by the antiferromagnetic gap $\omega_{k=0}^+$. Although the spin-wave description within the up-to-$O(S^3)$ approximation considerably underestimates the antiferromagnetic gap, its estimate $\omega_{k=0} = 2(S - s)J$ can be a qualitative guide. We learn that the antiferromagnetic gap is in proportion to $S - s$ and indeed find the slower activation and the higher-located peak of the antiferromagnetic component of $T^{-1}_f$ for $(S, s) = (\frac{3}{2}, \frac{1}{2})$ in comparison with those for $(S, s) = (1, \frac{5}{2})$ and $(S, s) = (\frac{3}{2}, 1)$. A careful observation of Fig. 3(a) shows that $T^{-1}_f$ reaches a minimum around $k_BT/J = 2.5$ for $(S, s) = (\frac{5}{2}, \frac{1}{2})$. In the two other cases, $T^{-1}_f$ is still on the decrease at $k_BT/J = 6.0$. We may understand whether $T^{-1}_f$ exhibits a minimum—that is to say, a ferromagnetic-to-antiferromagnetic crossover—at a tractable temperature in connection with the balance between the ferromagnetic band width $W^-$ and the antiferromagnetic gap $\Delta$. The ferromagnetic decreasing tail exists for $k_BT \lesssim W^-$, whereas the antiferromagnetic increasing behavior is remarkable for $k_BT \gtrsim \Delta$. If we evaluate $W^-$ and $\Delta$ as $\omega_{k=0}^- = -\omega_{k=0}^+ = 2JS$ and $\omega_{k=0}^+ = 2(S - s)J$, respectively, we may expect a detectable minimum of $T^{-1}_f$ as a function of temperature for $2s < S$. The larger $S - 2s$, the more pronounced crossover may be detected.

**IV. SUMMARY AND DISCUSSION**

A relaxation mechanism based on the interaction with spin waves has so far been applied to magnetic insulators only in a temperature range far below the onset of the long-range order [12]. We again stress that the present argument is a positive use of the spin-wave theory in one dimension in a temperature range above the onset of the (three-dimensional) long-range order. The quantum divergence of the spin reduction, inherent in one-dimensional antiferromagnets, no more plagues the present system, while we have avoided the thermal divergence of the bosonic distribution function modifying the spin-wave theory, that is, imposing a certain constraint on the magnetization. Though the present analysis must be a qualitative guide for the experiments over a wide temperature range, the description may be very precise especially for $k_BT/J \lesssim 0.2$. $T_1$ measurements at low temperatures and/or under high fields are strongly encouraged.

The experimental development depends on the synthesis of relevant materials. Although it is the pioneering measurements [22] on NiCu(pba)(H$_2$O)$_3$·2H$_2$O that have motivated the present study, the family compounds MCCu(pba)(H$_2$O)$_3$·2H$_2$O may not be so useful as to verify the present analysis. The linewidth in the NMR spectra for NiCu(pba)(H$_2$O)$_3$·2H$_2$O considerably broadens at low temperatures and therefore the extraction of $T_1$ was restricted to a temperature range $k_BT/J \gtrsim 0.5$, where it is rather hard for the present theory to make a quantitative interpretation, namely, a precise determination of the geometric parameters $A^2$ and $a^2$. Even though the linewidth broadening is inevitably dominated by the crystalline structure, a strong exchange coupling must be desirable here anyway. The idea of designing ligands capable of binding to two different metal ions with different donor atoms has not yet ended in an exchange coupling constant $J$ beyond $85$[cm$^{-1}$] $\approx 122k_B$[K] [27]. A breakthrough may be made by bringing into interaction metal ions and stable organic radicals. Ceneschi et al. [51] synthesized a series of ferrimagnetic chain compounds of general formula M(hfac)$_2$NITR, where metal ion complexes M(hfac)$_2$ with hfac = hexafluoroacetylacetone are bridged by nitronyl nitroxide radicals NITR. Their exchange coupling constants significantly vary with M and R but are in general fairly large in comparison with those of bimetallic chain compounds. An antiferromagnetic coupling of $313$[cm$^{-1}$] $\approx 450k_B$[K] was obtained for $M = Mn (S = \frac{5}{2})$ and $R = isopropyl (s = \frac{3}{2})$ [3]. While that of $424$[cm$^{-1}$] $\approx 610k_B$[K] for $M = Ni (S = 1)$ and $R = methyl (s = \frac{1}{2})$ [4]. Neither compound shows any transition to the three-dimensional magnetic order down to $k_BT/J = 0.02$, which is also suitable for our purpose, apart from designing a molecule-based ferromagnet. We theoreticians hope as many experimentalists as possible will take part in this exciting business-dynamic properties of one-dimensional quantum ferrimagnets.
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