Simulated nuclear spin-lattice relaxation in Heisenberg ferrimagnets: Indirect observation of quadratic dispersion relations

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In response to recent proton spin relaxation-time measurements on NiCu(pba)(H₂O)₃·2H₂O with pba = 1,3-propylenebis(oxamato), which is an excellent one-dimensional ferrimagnetic Heisenberg model system of spin-(1, 1/2), we study the Raman relaxation process in spin-(S, s) quantum ferrimagnets on the assumption of predominantly dipolar hyperfine interactions between protons and magnetic ions. The relaxation time \( T_1 \) is formulated within the spin-wave theory and is estimated as a function of temperature and an applied field \( H \) by a quantum Monte Carlo method. The low-temperature behavior of the relaxation rate \( T_1^{-1} \) qualitatively varies with \((S, s)\), while \( T_1^{-1} \) is almost proportional to \( H^{-1/2} \) due to the characteristic dispersion relations.

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Quantum spin chains have been providing broadband topics and have indeed invited numerous researchers to explore into them. One of the hot topics is the mixed-spin system with two kinds of antiferromagnetically exchange-coupled centers. Besides the competition between the massive and massless states [1] which is an interesting issue in itself, quantum ferrimagnetic phenomena have been attracting wide interest. There already exists an accumulated chemical knowledge on bimetallic chain compounds. Kahn et al. [3] succeeded in synthesizing the variety of ferrimagnetic bimetallic chains such as MCu(pba)(H₂O)₃·2H₂O (M = Mn, Ni) [3] and MCu(pbaOH)(H₂O)₃·2H₂O (M = Fe, Co, Ni) [4], where pba = 1,3-propylenebis(oxamato) and pbaOH = 2-hydroxy-1,3-propylenebis(oxamato). Under close contact between chemists and physicists, not only structural but also magnetic properties of them were elucidated [3]. It may be a few mathematical investigations [5, 6, 7] that renewed our enthusiasm toward the subject. Motivated by these works, several authors carried out spin-wave analyses [10, 11, 12] on the alternating-spin Heisenberg chains and pointed out the coexistence of the ferromagnetic and antiferromagnetic branches in the low-lying excitations. Modified spin-wave theories [11, 12] were further applied to the thermodynamics [13, 14] and a ferrimagnetic-to-antiferromagnetic crossover was found in the temperature dependences of the specific heat and the magnetic susceptibility. The dual structure of the excitations results in rich physics in a magnetic field as well, e.g., the double-peak structure of the specific heat [11] and quantized plateaux in the ground-state magnetization curve [10, 12]. Quantum ferrimagnetism and related phenomena are still central subjects in the field of material science. A family of one-dimensional oxides, Sr₃M'M'O₆ (M = Ni, Cu, Zn; M' = Pt, Ir), consisting of alternating M'O₆ octahedra and MO₆ trigonal prisms, visualizes the competition between various magnetic phases [13], whereas an ordered double perovskite, Sr₂FeMoO₆, acts as a half-metallic ferrimagnet [14, 15], exhibiting a novel magnetoresistive behavior.

In such circumstances, the proton spin relaxation time \( T_1 \) has recently been measured [21] for NiCu(pba)(H₂O)₃·2H₂O, which is typical of the spin-(1, 1/2) ferrimagnetic Heisenberg chain, in an attempt to reveal the electron-spin dynamics inherent in quantum ferrimagnets. Although the susceptibility-temperature product, \( \chi T \), shows a minimum in its temperature dependence (see Fig. 2 below), the observed relaxation rate \( T_1^{-1} \) is monotonically decreasing with the increase of temperature. The most interesting observation is the dependence of the relaxation rate on the applied magnetic field \( H \), which looks like \( T_1^{-1} \sim H^{-1/2} \), though the authors did not rule out a logarithmic behavior, \( T_1^{-1} \sim \ln H \), based on a rather approximate argument. We here present a rapid communication on our numerical simulation of \( T_1 \) all the more because the measurements reported are highly stimulative but still preliminary. We show that \( T_1 \) should indeed act as \( T_1^{-1} \sim H^{-1/2} \) for general spin-(S, s) ferrimagnetic Heisenberg chains due to the characteristic dispersion relations. The \( H^{-1/2} \)-dependence of \( T_1^{-1} \) may first remind us of the diffusive behavior of the spin correlation function [22]. However, a totally different mechanism may cause the field-dependent relaxation rate in the present system. Although the dynamic behavior [23] of quantum ferrimagnets is a fascinating subject, measurements in this direction seem to be still in their early stage. We expect the present calculation to accelerate experimental investigations into the dynamic properties.

We consider two kinds of spins \( S \) and \( s \) (\( S > s \)) alternating on a ring with antiferromagnetic exchange coupling between nearest neighbors, as described by the Hamiltonian

\[
\mathcal{H} = J \sum_{j=1}^{N} (S_j \cdot s_j + s_j \cdot S_{j+1}) - g \mu_B H \sum_{j=1}^{N} (S_j^z + s_j^z),
\]

(1)

where we have set the \( g \) factors of spins \( S \) and \( s \) both equal to \( g \). Keeping in mind ferrimagnetic bimetallic chain compounds such as NiCu(pba)(H₂O)₃·2H₂O [3], we
consider the proton spin relaxation of the two-magnon (Raman) type \[24\], which is usually the most dominant process due to the energy-conservation requirement for

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

where \(A_j^z\) and \(a_j^z\) are the coupling constants for the dipolar hyperfine interactions between protons and electron spins, \(\omega_N \equiv \gamma_N H\) is the Larmor frequency of the proton with \(\gamma_N\) being the gyromagnetic ratio, and the summation \(\sum_n\) is taken over all the eigenstates of \(|n\rangle\) with energy \(E_n\).

Let us introduce the spin-deviation operators within the linearized spin-wave theory \[9,10\] via \(S_j^\pm = \sqrt{2S}a_j^\mp\), \(S_j^z = S - a_j^z a_j^\dagger\), \(s_j^+ = \sqrt{2s}b_j^\dagger\), and \(s_j^- = -s + b_j b_j^\dagger\). Then the diagonalized spin-wave Hamiltonian without constant terms is represented as

\[
\mathcal{H} = \sum_k \left( \omega_k^- \alpha_k^\dagger \alpha_k + \omega_k^+ \beta_k^\dagger \beta_k \right),
\]

where \(\alpha_k\) and \(\beta_k\) describe the ferromagnetic and antiferromagnetic spin waves, respectively, and are related with the sublattice bosons via \(\alpha_k = a_k \sin\theta_k + b_k \cos\theta_k\) and \(\beta_k = \alpha_k^\dagger \sin\theta_k + b_k^\dagger \cos\theta_k\) with \(a_k = N^{-1/2} \sum_j e^{i\omega_j (j-1/4)} a_j, b_k = N^{-1/2} \sum_j e^{-i\omega_j (j+1/4)} b_j,\) and \(\tan(2\theta_k) = 2\sqrt{S}\cos(k/2)/(S + s)\). Here twice the lattice constant has been taken as unity. The dispersion relations are given by

\[
\omega_k^\pm = \omega_b \pm (S - s)J \mp g\mu_B H,
\]

with

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

Now, having in mind the significant difference between the electronic and nuclear energy scales \((\omega_N \lesssim 10^{-5}J)\), the relaxation rate can be expressed in terms of the spin waves as

FIG. 1. Temperature dependences of the proton spin relaxation rate at various values of the applied magnetic field: (a) \((S, s) = (1, \frac{1}{2})\), (b) \((S, s) = (\frac{3}{2}, \frac{1}{2})\), and (c) \((S, s) = (\frac{3}{2}, 1)\).

FIG. 2. Temperature dependences of the magnetic susceptibility times temperature for the Heisenberg ferrimagnetic chains of \(N = 32\), compared with the sums of those for the spin-\((S - s)\) ferromagnetic and spin-(2\(s\)) antiferromagnetic Heisenberg chains of \(N\) spins.
a certain constraint, for instance, on the magnetization, we can totally remove the difficulty and obtain a fine description of the thermodynamics [13], where it should be stressed that the dispersion (8) is still preserved. Thus, relying upon the Bogoliubov transformation, we perform the Monte Carlo sampling for the relevant spin operators

\begin{equation}
\begin{align*}
\alpha_k &= \frac{\cosh \theta_k}{\sqrt{2N}} \sum_j e^{i(k-\frac{1}{2}) S^z_j} + \sinh \theta_k \sum_j e^{i(k+\frac{1}{2}) S^+_j}, \\
\beta_k &= \frac{\sinh \theta_k}{\sqrt{2N}} \sum_j e^{-i(k-\frac{1}{2}) S^-_j} + \cosh \theta_k \sum_j e^{-i(k+\frac{1}{2}) S^-_j},
\end{align*}
\end{equation}

with the original compact Hamiltonian (1). While we base the relaxation process on the spin-wave excitations, we take grand-canonical averages within the original system. The thus-estimated \( n^{+}_k \) are indeed consistent with the exact calculations [23] of the dynamic structure factors \( S^{z}(k, \omega) = \sum_n (\langle n|S^{z}_k + S^{z}_k \rangle |g \rangle \langle g | \delta(\omega - E_n + E_k) \rangle \) through the relation \( n^{+}_k = \sum_\omega S^{z}(k, \omega) \), where \(|g \rangle \) is the ground state with energy \( E_k \) and magnetization \((S-s)N\). Since the applied field \( H \) is small enough in practice \( \langle g \mu_B H \lesssim 10^{-2} J \rangle \) [24], we neglect the Zeeman term of the Hamiltonian (1) in the numerical treatment. Considering the case of the contributing protons being located near the smaller-spin magnetic ions [3], we set \( A^z/a^z \) equal to 1/3.

We show in Fig. 2 the relaxation rate as a function of temperature. The calculations in the case of \((S,s) = (1,\frac{1}{2})\) are qualitatively consistent with the experimental observations [21], where \( T^{-1}_1 \) is a monotonically decreasing function of temperature. \( T^{-1}_1 \) hardly depends on temperature except for the effectively-low-temperature region satisfying \( k_B T \lesssim W^- \), where \( W^- \) is the ferromagnetic band width, which may qualitatively be identified with \( \omega^-_{k=\pi,-\omega=\theta} \). Considering the dispersion relations (8), it is convincing that the ferromagnetic, rather than antiferromagnetic, nature dominates the low-temperature relaxation process. In this context, we show in Fig. 3 the numerical calculations of \( \chi T \), which is closely related with \( T^{-1}_1 \) [24]. \( \chi T \) is a monotonically decreasing function in ferromagnets, while a monotonically increasing function in antiferromagnets. Thus we learn that ferrimagnets display the mixed behavior in their temperature dependences of \( \chi T \). Recently it has been pointed out [24] that Spin-(S,s) ferrimagnetic chains behave similar to combinations of spin-(S-s) ferromagnetic and spin-(2s) antiferromagnetic chains provided \( S = 2s \), which is again illustrated in Fig. 4. For \( S > 2s \), quantum ferrimagnets are predominantly ferromagnetic rather than antiferromagnetic, where \( \chi T \) more rapidly decreases than the, let us say, balanced behavior, \( \chi^{(S-s)\text{-ferro}} + \chi^{(2s)\text{-antiferro}} T \), whereas for \( S < 2s \), vice versa, where the low-temperature decrease is duller than the balanced behavior. It is quite interesting to observe Fig. 2 from this point of view. The relatively rapid
decrease of $T_1^{-1}$ at low temperatures for $(S, s) = (\frac{1}{2}, \frac{1}{2})$ must be of predominantly ferromagnetic aspect, while the shoulder-like, even increasing, behavior at low temperatures for $(S, s) = (\frac{3}{2}, 1)$ can be regarded as an anti-ferromagnetic feature. However, the overall gradual increase at high temperatures, as observed for $\chi T$, does not appear. It is the field-dependent prefactor to $n_k^\pm$ in Eq. (3), coming from the energy-conservation requirement $\delta(E_m - E_n - \omega_N)$ in Eq. (2), that suppresses the latent increasing behavior at high temperatures. Since $\omega_N \ll J$, the $k = 0$ component is predominant in the summation in Eq. (3). In general, with the increase of temperature, $n_k^\pm$ decrease in the vicinity of the zone center, whereas they increase near the zone boundary, where we note that $n_k^\pm$ both have their peaks at $k = 0$. Therefore, the increase of the field, reducing the predominance of the $k = 0$ component, smears out the temperature dependence of $T_1^{-1}$.

The characteristic prefactor in Eq. (3) further leads to the unique field dependence of $T_1^{-1}$. In Fig. 3 we plot $T_1^{-1}$ as a function of $\omega_N = \gamma_N H$. $T_1^{-1}$ is highly linear with respect to $H^{-1/2}$. We stress that the observations in Fig. 3 originate from the quadratic dispersion relations peculiar to this system and therefore the $H \to \infty$ extrapolation of $T_1^{-1}$ results in a considerably small value. Thus the present phenomena are distinguishable from the diffusive behavior, $\langle S_+^+ (t) S_-^- (0) \rangle \propto \exp(-D \gamma_N t)$, which also causes the field dependence of the form

$$\frac{1}{T_1} = P + Q \sqrt{\frac{J}{\gamma_N H}}. \quad (8)$$

The constant $P$ is inherent in the fluctuation-dominant spin dynamics. For $(\text{CH}_3)_4\text{NMnCl}_3$ and LiV$_2$O$_5$, which are both well known to be Heisenberg linear-chain compounds whose spin correlation functions behave diffusively at long times, $P/Q$ was estimated to be 139 (in the high-temperature limit) and 376 (at $k_B T / J \approx 0.65$), respectively. On the other hand, the spin-(1, 1) Heisenberg ferrimagnetic chain compound NiCu$_2$(pba)(H$_2$O)$_2$2H$_2$O exhibits $P/Q \approx 12$ (at $k_B T / J \approx 2.3$), which is much smaller than those of the spin-diffusive materials but is in good agreement with the present numerical findings (Table I). Therefore the $T_1$ measurements could implicitly demonstrate the low-energy quadratic dispersion relations of quantum ferrimagnets. When the XY-type exchange anisotropy moves the model away from the Heisenberg point, the chain turns critical, showing a linear dispersion, and the present field dependence of $T_1^{-1}$ should no more be expected. Thus the nuclear-magnetic-resonance, as well as neutron-scattering, measurements allow us to reveal the low-energy structure efficiently. We believe that the present calculations will greatly motivate further experimental investigations into quantum ferrimagnets.

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TABLE I. \( P/Q \) in the case of \( T_1 \) being fitted to \( T_1^{-1} = P + Q(\gamma N H/J)^{-1/2} \). The estimates in the limit of \( k_B T/J \to \infty \) are obtained through a rough extrapolation and are thus no more than for reference.

| \( k_B T/J \) | \( (1, \frac{1}{2}) \) | \( (\frac{3}{2}, \frac{1}{2}) \) | \( (2, 1) \) | (2.1) |
|---|---|---|---|---|
| 0.5 | 10.69 | 9.35 | 8.95 | 8.17 |
| 1.0 | 11.10 | 10.33 | 10.23 | 9.35 |
| 2.0 | 11.30 | 10.49 | 10.60 | 10.28 |
| 3.0 | 11.30 | 10.68 | 11.49 | 10.80 |
| 5.0 | 11.56 | 10.93 | 11.79 | 11.24 |
| \( \infty \) | 11.6 | 11.0 | 12.2 | 11.8 |