Nuclear spin relaxation in ordered bimetallic chain compounds

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A theoretical interpretation is given to recent proton spin relaxation-time ($T_1$) measurements on NiCu(C$_2$H$_4$N$_2$O$_4$)$_2$(H$_2$O)$_2$2H$_2$O, which is an ideal one-dimensional ferrimagnetic Heisenberg model system of alternating spins $1$ and $\frac{1}{2}$. The relaxation rate $T_1^{-1}$ is formulated in terms of the spin-wave theory and is evaluated by the use of a quantum Monte Carlo method. Calculations of the temperature and applied-field ($H$) dependences of $T_1^{-1}$ are in total agreement with the experimental findings. $T_1$ behaves as $T_1^{-1} \propto H^{-1/2}$, which turns out an indirect observation of the quadratic dispersion relations dominating the low-energy physics of quantum ferrimagnets.

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Recently considerable attention has been directed to ferrimagnetic mixed-spin chains. The simplest but practical example of a quantum ferrimagnet is two kinds of spins $S$ and $s$ alternating on a ring with antiferromagnetic exchange coupling between nearest neighbors. Because of the noncompensating sublattice magnetizations, this system exhibits ferrimagnetically degenerate ground states [1]. Thus, in contrast with ferromagnets and antiferromagnets, ferrimagnets show the ground-state excitations of dual aspect [2]. The elementary excitations of ferromagnetic features, reducing the ground-state magnetization, form a gapless dispersion relation, whereas those of antiferromagnetic features, enhancing the ground-state magnetization, are gapped from the ground state. The two distinct low-lying excitations result in the unique thermal behavior which contains both ferromagnetic and antiferromagnetic aspects [2][3].

Quantum ferrimagnets in a magnetic field provide further interesting topics such as the double-peak structure of the specific heat [7] and quantized plateaux in the ground-state magnetization curves [8][10].

The first ferrimagnetic one-dimensional compound, MnCu(dto)$_2$(H$_2$O)$_2$·4.5H$_2$O (dto = dithiooxalato = $S_2C_2O_5$), was synthesized by Gleizes and Verdugue [11]. Their pioneering efforts, combined with semiclassical but enlightening calculations, successfully characterized the one-dimensional ferrimagnetic behavior [12]. Another example of an ordered bimetallic chain, MnCu(pba)(H$_2$O)$_3$·2H$_2$O (pba = 1,3-propylenebis(oxamato) = $C_7H_6N_2O_6$), was provided by Pei et al. [13] and turned out to exhibit more pronounced one dimensionality. Kahn et al. [14] further synthesized the family of related compounds systematically, focusing on the problem of the crystal engineering of a molecule-based ferrimagnet—the assembly of the highly magnetic molecular entities within the crystal lattice in a ferrimagnetic fashion. There also appeared an idea [15] that the alternating magnetic centers do not need to be metal ions but may be organic radicals.

In comparison with the accumulated chemical knowledge and well-revealed static properties introduced above, the dynamic properties of quantum ferrimagnets have much less been studied so far. To the best of our knowledge, it was not until quite recently that the dynamic structure factors were calculated [16], whereas any direct observation of the dispersion curves is not yet so successful, for instance, as that [17] for the Haldane antiferromagnets [18]. While Caneschi et al. [19] performed electron-paramagnetic-resonance measurements on novel ferrimagnetic compounds, which consist of alternating metal ions and stable organic radicals, they focused their analyses on the relation between the spectra and short-range correlation effects. In such circumstances, the proton spin relaxation time $T_1$ has quite recently been measured [15] for the spin-($1\frac{1}{2}$) ferrimagnetic Heisenberg chain compound, NiCu(pba)(H$_2$O)$_3$·2H$_2$O, where the dependence of the relaxation rate $T_1^{-1}$ on the applied magnetic field $H$ looks like $T_1^{-1} \propto H^{-1/2}$, though the authors’ semiquantitative approximate argument has reached a logarithmic behavior, $T_1^{-1} \sim \ln H$, rather than the observations. Motivated by this stimulative experiment, we here discuss the nuclear spin relaxation peculiar to ordered bimetallic chain compounds in connection with their energy structure. Formulating the relaxation process based on the spin-wave theory, we perform numerical evaluation of $T_1^{-1}$. Investigating the dependences of $T_1^{-1}$ on temperature and the applied field, we demonstrate that the $T_1$ measurement is nothing but an indirect observation of the characteristic elementary excitations of quantum ferrimagnets.

The ferrimagnetic material NiCu(pba)(H$_2$O)$_3$·2H$_2$O [13] consists of ordered bimetallic chains with alternating octahedral Ni$^{2+}$ and square-pyramidal Cu$^{2+}$ ions bridged by oxamato groups. The chain runs along the $b$-axis of the orthorhombic lattice whose space group is $Pnma$ and is described by the Hamiltonian

$$\mathcal{H} = J \sum_{j=1}^{N} (\mathbf{S}_j \cdot \mathbf{s}_j + \mathbf{s}_j \cdot \mathbf{S}_{j+1}) - g\mu_B H \sum_{j=1}^{N} (S_j^z + s_j^z),$$

(1)

where we have set the $g$ factors of spins $S = 1$ and $s = \frac{1}{2}$ both equal to $g$ because the difference between them amounts to at most several per cent of themselves in prac-
The high-temperature susceptibility measurements suggest that $J \approx 121$K. The one dimensionality is well exhibited above about 7K. Due to the energy-conservation requirement for the electronic-nuclear spin system, 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 [21].

Neglecting the higher-order relaxation process, the relaxation rate is generally represented as

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

where $A_j^z$ and $a_j^\dagger$ are the dipolar coupling constants between the proton and electron spins in the $j$th unit cell, $\omega_N \equiv \gamma_N H$ is the Larmor frequency of $^1$H 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 bosonic spin-deviation operators $S_j^z = \sqrt{2S} a_j^z$, $S_j^z = S - a_j^\dagger a_j$, $s_j^z = \sqrt{2S} b_j^z$, and $s_j^z = -s + b_j^\dagger b_j$. The Bogoliubov transformation

$$\alpha_k = \cosh \theta_k a_k + \sinh \theta_k b_k^\dagger,$$

$$\beta_k = \sinh \theta_k a_k^\dagger + \cosh \theta_k b_k,$$

with

$$a_k = \frac{1}{\sqrt{N}} \sum_j e^{ik(j-1/2)} a_j,$$

$$b_k = \frac{1}{\sqrt{N}} \sum_j e^{-ik(j+1/2)} b_j,$$

and

$$\tanh(2\theta_k) = 2\sqrt{S_s} \cos \left(\frac{k}{2}\right),$$

diagonalizes the Hamiltonian [2], discarding the constant terms, as

$$H = \sum_k \left( \omega_k^- \alpha_k^\dagger \alpha_k + \omega_k^+ \beta_k^\dagger \beta_k \right),$$

where $\alpha_k^\dagger$ and $\beta_k^\dagger$ are the creation operators of the ferromagnetic and antiferromagnetic spin waves of momentum $k$ whose dispersion relations are given by

$$\omega_k^\pm = J \sqrt{(S-s)^2 + 4S_s \sin^2(k/2)} + (S-s)J \mp g\mu_B H,$$

with twice the lattice constant being taken as unity. In terms of the spin waves, the relaxation rate [3] is expressed as

$$\frac{1}{T_1} = \frac{4\pi \hbar}{N^2} (g\mu_B\gamma_N)^2 \sum_{k, q} \sum_{\sigma = \pm} \delta(\omega_{k+q}^\sigma - \omega_{k}^\sigma - \hbar\omega_N) \times \left[ (A_j^z \cosh \theta_k c_j a_j^\dagger + \sinh \theta_k c_j s_j^z) n_{k+q}^\sigma (n_{k}^\sigma + 1) + (a_j^\dagger s_j^z \sinh \theta_k c_j a_j^\dagger) n_{k}^\sigma (n_{k+q}^\sigma + 1) - 2A_j^z (\cosh \theta_k c_j a_j^\dagger) n_{k}^\sigma (n_{k+q}^\sigma + 1) \right],$$

where $n_k^- \equiv \langle a_k^\dagger a_k \rangle$ and $n_k^+ \equiv \langle \beta_k^\dagger \beta_k \rangle$ are the thermal averages of the numbers of the spin waves at a given temperature, and $A_j^z = \sum_j e^{i(q-1/4)} A_j^z$ and $a_j^\dagger = \sum_j e^{i(q+1/4)} a_j^\dagger$ 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. (8) ends in

$$\frac{1}{T_1} = \frac{4\hbar}{N J} (g\mu_B\gamma_N)^2 \sum_k \sqrt{(Ssk)^2 + 2(S-s)Ss \hbar\omega_N/J} \times \left[ (A^z \cosh \theta_k s_j^z - a^z \sinh \theta_k s_j^z) n_{k}^-(n_{k}^+ + 1) + (A^z \sinh \theta_k s_j^z - a^z \cosh \theta_k s_j^z) n_{k}^+(n_{k}^- + 1) \right],$$

where we have assumed little $k$-dependence of $A_j^z$ and $a_j^\dagger$, and thus replaced $A_j^z = A_{j=0}^z$ and $a_j^\dagger = a_{j=0}^\dagger$ by $A^z \equiv A_{j=0}^z$ and $a^\dagger \equiv a_{j=0}^\dagger$, respectively.

Now we have an idea of evaluating the thermal averages $n_k^\pm$ by a quantum Monte Carlo method. Though the divergence of the ground-state sublattice magnetization, which plagues the spin-wave treatment of low-dimensional antiferromagnets, does not persist in our model, $n_k^\pm$ still diverge as temperature increases as far as we naively estimate them with the noncompact bosonic Hamiltonian [2].

On the other hand, we are fully allowed to rely upon the dispersion relations [2] themselves even at finite temperatures, because we can efficiently modify the spin-wave thermodynamics [2] so as to describe the higher-temperature behavior introducing an additional constraint on the magnetization but preserving the linearized spin-wave dispersions $\omega_k^\pm$. Thus, depending on the Bogoliubov transformation [3] but avoiding the direct estimation of the boson numbers, we perform the Monte Carlo sampling for the relevant spin operators

$$\alpha_k = \frac{\cosh \theta_k}{\sqrt{2N}} \sum_j e^{ik(j-1/2)} S_j^z + \frac{\sinh \theta_k}{\sqrt{N}} \sum_j e^{ik(j+1/2)} s_j^z,$$

$$\beta_k = \frac{\sinh \theta_k}{\sqrt{2N}} \sum_j e^{-ik(j-1/2)} S_j^- + \frac{\cosh \theta_k}{\sqrt{N}} \sum_j e^{-ik(j+1/2)} s_j^-,$$

with the original compact Hamiltonian [2]. While we base the relaxation process on the spin-wave excitations, we take grand-canonical averages within the original system. Since the applied field $H$ is so small as to satisfy $g\mu_B H \lesssim 10^{-2} J$, we neglect the Zeeman term of the...
Hamiltonian (1) in the numerical treatment. The thus-calculated structure factors \( n_{\pm}^k \) are shown in Fig. 1. \( n_{\pm}^k \) both have their peaks at \( k = 0 \) in the reduced Brillouin zone, which reflects the combination of the ferromagnetic and antiferromagnetic features. The momentum dependencies of \( n_{\pm}^k \) well support the characteristic Schottky-like peak of the specific heat \( C \), where the ferromagnetic structure is rapidly smeared out as temperature increases, while the antiferromagnetic one still persists at rather high temperatures. Therefore the present analysis is promising. The dipolar coupling is quite sensitive to the location of the proton because the coupling strength is proportional to \( r^{-3} \) with \( r \) being the distance between the interacting proton and electron spins. In the experiment on \( \text{NiCu(pba)}(\text{H}_2\text{O})_3\cdot2\text{H}_2\text{O} \), it has been demonstrated \([19]\) that the protons mainly contributing to \( T_1^{-1} \) lie in the pba groups rather than the \( \text{H}_2\text{O} \) molecules and are therefore all located beside Cu ions. Hence we here reasonably neglect \( A_z \) in comparison with \( a^z \). Setting \( a^z = 6.12 \times 10^{-3} [\text{Å}^{-3}] \) with \( g = 2 \), the calculations successfully reproduce the observations.
in mono-spin chains, now shifts to the zone center due to
the double periodicity in the present system. With
the increase of temperature, the structure factor generally
decreases in the vicinity of its peaks, while it increases
in its lower slopes. Thus, due to the predominance of the
$k = 0$ component in the summation (1), $T_1^{-1}$ ends up as a
decreasing function of temperature. The increase of the
applied field, having an effect of reducing the predomi-
nance of the $k = 0$ component, relaxes the pronounced
decreasing behavior of $T_1^{-1}$ as a function of temperature
and would possibly allow $T_1^{-1}$ to show a reversed but
weak temperature dependence at high temperatures.

Another interesting observation is the field dependence
of the relaxation rate shown in Fig. 3. $T_1^{-1}$ looks
almost linear with respect to $H^{-1/2}$, which also suggests
that only the magnons of $k \approx 0$ effectively contribute to
the relaxation process. We stress that the present field
dependence comes from the energy-conservation require-
ment $\delta(E_m - E_n - \hbar \omega_N)$ in Eq. (2), that is, from the
quadratic dispersion relations of the elementary excita-
tions. In this context, the spin-diffusion effect (12) may
be mentioned, which also results in a similar field depen-
dence of $T_1^{-1}$,

$$
\frac{1}{T_1} = P + \frac{Q}{\sqrt{H}},
$$

(11)

where $P$ arises from longitudinal spin fluctuations,
whereas the field-dependent term originates from
transverse spin fluctuations which are diffusive at high
lengths and long times. For $\text{CH}_3\text{NMeCl}_3$ [24]
and LiV$_2$O$_3$ [25], which are both well known to be spin-

The present compound, NiCu(pba)(H$_2$O)$_3$.2H$_2$O, is
reasonably described by the isotropic Heisenberg Hamil-
tonian. There exist a series of family compounds [11–14]
and thus the prototypical ferrimagnetic behavior [20]
could potentially be elucidated as a function of the con-
stituent spins. The consideration of anisotropy effects
may also be interesting from the practical point of view.
For the anisotropic Hamiltonian

$$
H = J \sum_j [(S_j \cdot s_j) + (s_j \cdot S_{j+1})_1 + \sum_j [D_S(S_j^2) + D_s(s_j^2)] - g\mu_B H \sum_j (S_j^2 + s_j^2),
$$

(12)

with $(S \cdot s)_1 = S^z s^z + S^y s^y + \alpha S^z s^z$, the relaxation rate (3) is replaced by

$$
\frac{1}{T_1} = \frac{4\hbar}{N J} (g\mu_B \gamma_N)^2 \sum_k \frac{f_{S,s}(\alpha, D_S, D_s)}{(\Delta k)^2 + 2Ss \sum_{\alpha, D_S, D_s} \hbar \omega_N / J} \times \left[ (A^2 \cosh^2 \theta_k - a^2 \sinh^2 \theta_k) n_k^+ (n_k^- + 1) + (A^2 \sinh^2 \theta_k - a^2 \cosh^2 \theta_k) n_k^- (n_k^+ + 1) \right],
$$

(13)

where

$$
f_{S,s}(\alpha, D_S, D_s) = \sqrt[\alpha(S + s) - (SD_S + sD_s)/J^2 - 4Ss].
$$

(14)

Even if any anisotropy of the easy-axis type is introduced,
the small-momentum quadratic dispersion remains qual-
itatively unchanged and thus the characteristic field
dependence of the relaxation rate, $T_1^{-1} \propto H^{-1/2}$, should
still be observed, where the slope $\partial T_1^{-1}/\partial H^{-1/2}$ gives
semiquantitative information on the anisotropy. How-
ever, the expression (13) is no more valid under the easy-
plane type anisotropy. The model indeed turns critical
for $\alpha < 1$, showing linear dispersion relations [24].
Therefore ferrimagnetic compounds with anisotropic inter-
actions of the easy-plane type should exhibit no field depen-
dence of $T_1^{-1}$. Thus the nuclear magnetic resonance is all
the more efficient to investigate the low-energy structure
in the present system. We really hope that the present
successful interpretation of the pioneering experiments
will stimulate and accelerate further study on this fasci-
nating system. The developed calculations under various
 constituent spins and geometric parameters will be pre-
sented elsewhere [25].

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