Significance of the direct relaxation process in the low-energy spin dynamics of a one-dimensional ferrimagnet NiCu(C<sub>7</sub>H<sub>6</sub>N<sub>2</sub>O<sub>6</sub>)(H<sub>2</sub>O)<sub>3</sub>·2H<sub>2</sub>O

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In response to recent nuclear-magnetic-resonance measurements on a ferrimagnetic chain compound NiCu(C<sub>7</sub>H<sub>6</sub>N<sub>2</sub>O<sub>6</sub>)(H<sub>2</sub>O)<sub>3</sub>·2H<sub>2</sub>O [Solid State Commun. 113 (2000) 433], we calculate the nuclear spin-lattice relaxation rate 1/T<sub>1</sub> in terms of a modified spin-wave theory. Emphasizing that the dominant relaxation mechanism arises from the direct (single-magnon) process rather than the Raman (two-magnon) one, we explain the observed temperature and applied-field dependences of 1/T<sub>1</sub>. Ferrimagnetic relaxation phenomena are generally discussed and novel ferrimagnets with extremely slow dynamics are predicted.

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I. INTRODUCTION

Design of molecule-based ferromagnets has been one of the most exciting subject in Materials science. One can in principle obtain molecular ferromagnets by assembling molecular bricks so as to construct a low-dimensional system with a magnetic ground state and then coupling the chains or the layers again in a ferromagnetic fashion [1]. In the naïvest attempt to obtain a magnetic ground state, we may couple the nearest-neighbor magnetic centers ferromagnetically [2]. However, it is often difficult to realize the symmetry conditions favoring the parallel alignment of local spins. The difficulty was overcome by the introduction of a new concept—antiferromagnetically coupled polymetallic systems with irregular spin-state structures [3]. Ordered bimetallic chain compounds were thus synthesized and since then the magnetic properties of ferrimagnetic Heisenberg chains have extensively been investigated [4,10].

Recently nuclear magnetic resonance for <sup>1</sup>H nuclei has been performed in a ferrimagnetic chain compound and stimulative temperature and applied-field dependences of the proton spin-lattice relaxation rate 1/T<sub>1</sub> has been reported [1]. The authors analyzed 1/T<sub>1</sub> in terms of the naïve spin-wave theory [12] but could not successfully interpret the characteristic field dependence, which looks like 1/T<sub>1</sub> ∝ 1/√T<sub>1</sub>. We here point out that their argument broke down because they attributed the dominant relaxation mechanism to the Raman (two-magnon) process. Modifying the naïve spin-wave theory so as to fully describe the thermodynamics, we demonstrate that the direct (single-magnon) relaxation process can be effective in Heisenberg ferrimagnets. We further discuss potential ferrimagnetic spin dynamics arising from the characteristic twofold excitations [13].

II. SPIN-WAVE APPROACH

The measured compound NiCu(pba)(H<sub>2</sub>O)<sub>3</sub>·2H<sub>2</sub>O (pba = 1,3-propylenebis(oxamato) = C<sub>7</sub>H<sub>6</sub>N<sub>2</sub>O<sub>6</sub>) [14] consists of ordered bimetallic chains with alternating octahedral Ni<sup>2+</sup> and square-pyramidal Cu<sup>2+</sup> ions bridged by oxamato groups. The one-dimensional character holds down to 7[K] under the exchange coupling J/k<sub>B</sub> ≃ 121[K]. The g factors of the S = 1 and s = 1/2 spins are both close to 2 [15]. Thus the material is reasonably described by the one-dimensional mixed-spin Heisenberg Hamiltonian

\[ \mathcal{H} = J \sum_{j=1}^{N} (\mathbf{S}_j \cdot \mathbf{s}_j + \mathbf{s}_j \cdot \mathbf{S}_{j+1}) - g\mu_B H \sum_{j=1}^{N} (S^z_j + s^z_j), \]

where \( \mathbf{S}_j \) and \( \mathbf{s}_j \) are respectively spin-S(= 1) and spin-s(= 1/2) operators at the \( j \)th elementary cell. The spin-lattice relaxation rate is given by

\[ \frac{1}{T_1} = \frac{4\pi(g\mu_B\hbar\gamma_N)^2}{\hbar} \sum_{n,m} e^{-E_n/k_B T} \sum_{n,m} \delta(E_m - E_n - \hbar\omega_N), \]

where \( \omega_N \equiv \gamma_N H \) is the Larmor frequency of the nuclei with the gyromagnetic ratio \( \gamma_N \) and the summation \( \sum_n \) is taken over all the electronic eigenstates \( |n\rangle \) with energy \( E_n \). Assuming the hyperfine interaction to be isotropic, we may represent \( \mathcal{H}_{\text{int}} \) as

\[ \mathcal{H}_{\text{int}} = \sum (A\mathbf{I}_j \cdot \mathbf{S}_j + B\mathbf{I}_j \cdot \mathbf{s}_j), \]

with the nuclear spin operators \( \mathbf{I}_j \) and the dipolar coupling constants \( A \) and \( B \).

In order to calculate 1/T<sub>1</sub> in practice, we introduce the bosonic operators for the spin deviation as

\[ S^+_j = (2S - a_j^+a_j)^{1/2}a_j, \quad S^z_j = S - a_j^+a_j, \]
\[ s^+_j = b_j^+(2s - b_j^+b_j)^{1/2}, \quad s^z_j = -s + b_j^+b_j. \]

Then, assuming \( O(S) = O(s) \), we can expand \( \mathcal{H}_{\text{int}} \) with respect to 1/S and obtain 1/T<sub>1</sub> = \( \sum_{l=1,2,\ldots} 1/T_1^{(l)} \).
where $1/T_1^{(l)}$ is the $l$-magnon relaxation rate within the first-order spin-lattice relaxation process and is given by replacing $H_{\text{int}}$ by its $O(S^{1-1/2})$-component in Eq. (3). On the other hand, within the up-to-$O(S^0)$ approximation, the electronic Hamiltonian (4) can be diagonalized as

$$H \approx H_{SW} = E_g + \sum_k \left( \bar{\omega}_k^- \alpha_k^+ \alpha_k + \bar{\omega}_k^+ \beta_k^+ \beta_k \right).$$

Here, $E_g$ is the spin-wave ground-state energy, whereas $\alpha_k^+$ and $\beta_k^+$ create the spin waves of ferromagnetic and antiferromagnetic aspects [18], respectively, and are related with the sublattice bosons via $\alpha_k^+ = a_k^+ \cosh \theta_k + b_k^+ \sinh \theta_k$ and $\beta_k^+ = a_k^+ \sinh \theta_k + b_k^+ \cosh \theta_k$ with $a_k^+ = (1/\sqrt{N}) \sum_j e^{-ik(j-1/4)} a_j^+$, $b_k^+ = (1/\sqrt{N}) \sum_j e^{ik(j+1/4)} b_j^+$, and $\tanh(2 \theta_k) = 2 \sqrt{S \cos(k/2)/(S + s)}$. We here take twice the lattice constant as unity. The dispersion relations are given by

$$\bar{\omega}_k^\pm = \omega_k^\pm - \delta \omega_k^\pm,$$

where

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

$$\delta \omega_k^\pm = 2(S + s) \Gamma_1 \sum_k \frac{\sin^2(k/2)}{\omega_k} - \frac{\Gamma_2}{\sqrt{S}} [\omega_k \pm (S - s)],$$

with

$$\omega_k = J \sqrt{(S-s)^2 + 4S \sin^2(k/2)},$$

$$\Gamma_1 = \frac{1}{2N} \sum_k \left( \frac{S + s}{\omega_k} - 1 \right),$$

$$\Gamma_2 = \frac{1}{N} \sum_k \sqrt{S \cos^2(k/2)} / \omega_k.$$  

The linear spin waves are characterized by $\omega_k^\pm$, while the interacting spin waves by $\bar{\omega}_k^\pm$ with the $O(S^0)$ quantum corrections $\delta \omega_k^\pm$. We plot $\bar{\omega}_k^\pm$ and $\omega_k^\pm$ in Fig. 1. The spin waves describe the elementary excitations satisfactorily, especially the low-energy excitations near the zone center, which must be the most relevant to the nuclear spin relaxation. The antiferromagnetic excitation energies are underestimated by the linear spin waves but are significantly corrected in consideration of the interactions between them. All the following calculations are based on the interacting-spin-wave dispersions $\bar{\omega}_k^\pm$.

The $\delta$ function in Eq. (3) insures the conservation of energy in the transition. Considering the significant difference between the electronic and nuclear energy scales ($\hbar \omega_N \lesssim 10^{-5} J$), the relevant spin-wave excitations are strongly limited. Only the small-momentum ferromagnetic spin waves contribute to the direct process. In the Raman process, both ferromagnetic and antiferromagnetic spin waves are effective but interband transitions are still irrelevant. Scatterings between ferromagnetic and antiferromagnetic spin waves are relevant to the higher-order processes containing three or more magnons. We show a few leading terms of the relaxation rate:

$$\frac{1}{T_1^{(1)}} \approx \frac{4(\mu_B \hbar \gamma N)^2}{N J h} \sqrt{\frac{2(S-s)}{S \hbar \omega_N J}} \times (\sqrt{S} \cosh \theta_0 - \sqrt{S} \sinh \theta_0)(n_0^0 + 1),$$  

$$\frac{1}{T_1^{(2)}} \approx \frac{\sum_k N J h \sqrt{(S \omega_k^2 + 2(S - s) S \hbar \omega_N J)}}{4(\mu_B \hbar \gamma N)^2 (S - s)} \times (\cosh^2 \theta_k - B \sinh^2 \theta_k)(n_k^- + 1) + (\sinh^2 \theta_k - B \cosh^2 \theta_k)(n_k^+ + 1)],$$

$$\frac{1}{T_1^{(3)}} \approx \sum_k \frac{2N J h \sqrt{S \omega_k^2 + 2(S - s) S \hbar \omega_N J}}{2N \hbar \omega_k^2 + 2(S - s) S \hbar \omega_N J} \times \left[ \left( \frac{A}{\sqrt{S}} \sinh \theta_k \sinh \theta_k' \sinh \theta_{k+k'}^+ - \frac{B}{\sqrt{S}} \sinh \theta_k \sinh \theta_k' \sinh \theta_k^+ \sinh \theta_{k+k'}^+ \right) n_k^- n_k'^+ \right] + 4 \left( \frac{A}{\sqrt{S}} \cosh \theta_k \cosh \theta_k' \cosh \theta_{k+k'}^+ - \frac{B}{\sqrt{S}} \cosh \theta_k \cosh \theta_k' \cosh \theta_k^+ \cosh \theta_{k+k'}^+ \right) n_k^- n_k'^+ \sinh \theta_k \sinh \theta_k' \sinh \theta_k^+ \sinh \theta_{k+k'}^+, \right. \]

where $n_k^- \equiv \langle \alpha_k^+ \alpha_k \rangle$ and $n_k^+ \equiv \langle \beta_k^+ \beta_k \rangle$ are the distribution functions of the spin waves. In general $1/T_1^{(l)}$ rapidly decreases as a function of $l$. However, a slight anisotropy, for example, turns off the direct process and therefore makes the Raman process effective. In such a case, the three-magnon-process relaxation rate can also be effective, being enhanced via the exchange interaction, at high temperatures [16-19].
Now the problem is reduced to the evaluation of \( n_k^\pm \). The naivest thermodynamics defining the partition function as \( Z = \text{Tr}[e^{-\mathcal{H}_{SW}/k_B T}] \) ends in the divergence of \( n_k^\pm \) with increasing temperature. Thus we here employ the modified spin wave theory for ferrimagnets [17,20] and obtain the spin-wave distribution functions as

\[
n_k^\pm = \frac{1}{e^{[\omega_k^\pm - \mu(S+s)/\hbar \omega_k]/k_B T} - 1}, \tag{15}
\]

where \( \mu \) is a Lagrange multiplier controlling the staggered magnetization and is self-consistently determined under the constraint \( \sum_k \sum_{\sigma = \pm} n^\sigma_k / \omega_k = N \). We show in Fig. 2 the thus-obtained \( n_k^\pm \) as functions of \( k \). At low temperatures, \( n_k^- \) exhibits a pronounced peak at \( k = 0 \), whereas \( n_k^+ \) stays negligibly small in comparison with \( n_k^- \), because the ferromagnetic and antiferromagnetic excitations are respectively gapless and gapped from the ground state. Even at high temperatures, \( n_k^- \) remains less dominant due to the large gap \( \omega_k^- = 2J(S-s)(1 + \Gamma_2/\sqrt{8S}) \) with \( \Gamma_2 = 0.4777 \) for \( (S,s) = (1,\frac{1}{2}) \). The applied field, slightly shifting the spin-wave excitation energies, reduces \( n_k^- \) and enhances \( n_k^+ \).

Let us observe general behavior of \( 1/T_1 \) in Fig. 3. We have learned in Fig. 2 that the ferromagnetic and antiferromagnetic spin waves respectively contribute decreasing and increasing components as functions of temperature to the relaxation rate. Therefore, \( 1/T_1^{(1)} \) results in a monotonically decreasing function of \( T \), whereas \( 1/T_1^{(2)} \) contains increasing components as well as overwhelming decreasing ones. Here is a fascinating parameter to be adjusted, \( r \equiv A/B \). Dipolar coupling constants are proportional to the inverse cube of the distance between the interacting nuclear and electronic spins and therefore \( r \) is quite sensitive to the crystalline structure. Considering the predominance of the small-momentum excitations, we find there is a special point of \( r = s/S \), where the dominant relaxation mechanism mediated by the ferromagnetic spin waves does not work at all in every magnon process and thus the Raman process mediated by the antiferromagnetic spin waves becomes the leading relaxation mechanism. That is why as \( r \) approaches \( s/S \), the Raman contribution increases emphasizing the increasing behavior as a function of \( T \).

**Fig. 2.** The momentum distribution functions of the ferromagnetic (a) and antiferromagnetic (b) spin waves at various values of temperature and the applied magnetic field in the case of \( (S,s) = (1,\frac{1}{2}) \).

**Fig. 3.** Temperature dependences of the direct-process and Raman-process relaxation rates at various values of the applied magnetic field in the case of \( (S,s) = (1,\frac{1}{2}) \). \( 1/T_1^{(1)} \) is plotted by thin lines, while \( 1/T_1^{(1)} + 1/T_1^{(2)} \) by thick lines.

### III. Explanation of the Experiment

We apply the theory to the proton spin relaxation [17] in NiCu(pba)(H₂O)₃·2H₂O. Since the protons mainly contributing to \( 1/T_1 \) turn out to lie in the pba groups near Cu ions, we hear set \( r \) smaller than unity.
We analyze the observed temperature dependences of $1/T_1$ [11] in Fig. 4. Though no parametrization ends in a total agreement with the measurements, the calculation can reproduce them fairly well. In the present sample, the relevant protons have a rather wide distribution around Cu ions and therefore the distances between the interacting proton and electron spins, which we refer to as $a$ and $b$ for $S = 1$ and $s = 1/2$, respectively, can not be determined definitely. If we assume that $A \sim 1/a^3$ and $B \sim 1/b^3$, $4.48 \times 10^{-3}[\text{Å}^{-3}]$ for $B$ may be too small, while 0.4 for $r$ be too large. As the applied field increases, the recovery curve of the spin-echo decay more and more deviates from a single-exponential function [21]. The experimental estimates of $1/T_1$ at $H \gtrsim 1$[T] seem to contain larger uncertainty.

Field dependence of $1/T_1$ was measured in more detail at 280[K] [11] and is analyzed in Fig. 4. We again find that the calculations with small $r$ can generally be fitted to the measurements. We emphasize that the linear dependence of $1/T_1$ on $1/\sqrt{H}$ with a steep slope can never be attributed to the Raman process but be described in consideration of the direct process. As the most significant field dependence is obtained at $r = 0$ in each relaxation process, the Raman contribution to the field dependence turns out much smaller than that from the direct process. The three-magnon contribution, even if it is enhanced via the exchange interaction, is still less relevant. In general, the momentum integral in the calculation of $1/T_1$ weakens the linear field dependence and even leads to logarithmic one at high fields.

We should be reminded that the present spin-wave theory, which is free from both quantum and thermal divergences of the sublattice magnetizations, is highly successful but its ability to describe thermodynamics is still restricted quantitatively [18]. Considering minor corrections to the theory as well, arising from distribution of proton spins, slight difference between $g$ factors, weak interchain interactions and so forth, we are allowed to conclude that the direct process plays a leading role in the nuclear spin relaxation of NiCu(pba)(H$_2$O)$_3\cdot$2H$_2$O.

**IV. CONCLUDING REMARKS**

The dominant relaxation mechanism for the title compound has been shown to arise from the direct process. It is at the same time the demonstration that the material is a really isotropic magnet.

Another harvest we have obtained is the prediction of novel ferrimagnets with extremely slow dynamics. Under the crystalline structure with $r = s/S$, the fast relaxation processes mediated purely by the ferromagnetic spin waves hardly work and thus the nuclear spin is very slow in relaxing especially at low temperatures.

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