Modified Spin-Wave Theory of Nuclear Magnetic Relaxation in One-Dimensional Quantum Ferrimagnets: Three-Magnon versus Raman Processes

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Nuclear spin-lattice relaxation in one-dimensional Heisenberg ferrimagnets is studied by means of a modified spin-wave theory. Calculating beyond the first-order mechanism, where a nuclear spin directly interacts with spin waves through the hyperfine coupling, we demonstrate that the exchange-scattering-enhanced three-magnon nuclear relaxation may generally predominate over the Raman one with increasing temperature and decreasing field. Recent proton spin-lattice relaxation-time ($T_1$) measurements on the ferrimagnetic chain compound NiCu(C$_7$H$_6$N$_2$O$_4$)(H$_2$O)$_3$·2H$_2$O suggest that the major contribution to $1/T_1$ be made by the three-magnon scattering.

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I. INTRODUCTION

Nuclear magnetic resonance (NMR) is an effective probe to the collective motions of electronic spins and therefore we take a great interest in microscopically interpreting it. The spin-wave formalism has played a crucial role in this context. Van Kranendonk, Bloom, and Moriya made their pioneering attempts to describe the nuclear spin-lattice relaxation time $T_1$ in terms of spin waves. Oguchi and Keffer further developed the spin-wave analysis considering the three-magnon nuclear relaxation mechanism as well as the Raman one. Pincus and Beeman claimed that the exchange correlation between spin waves should significantly accelerate the nuclear spin relaxation. The spin-wave excitation energy is usually much larger than the nuclear resonance frequency and thus the single-magnon relaxation process is rarely of significance. The Raman process consequently plays a leading role in the nuclear spin-lattice relaxation. Because of the $(4S)^{-1}$-damping factor to the Holstein-Primakoff magnon series expansion, the multi-magnon scattering is much less contributive within the first-order process, where a nuclear spin directly interacts with spin waves through the hyperfine coupling. However, the second-order process, where a nuclear spin flip induces virtual spin waves which are then scattered thermally via the four-magnon exchange interaction, may generally enhance the relaxation rate. This is the fascinating scenario written by Pincus and Beeman.

It is unfortunate that their spin-wave nuclear relaxation theory is not effective in low dimensions but is valid far below the transition temperature. The conventional spin-wave theory applied to low-dimensional magnets ends in failure with diverging magnetizations. In such circumstances, Takahashi gave a fine description of the low-dimensional ferromagnetic dynamics in terms of modified spin waves. His idea of introducing a constraint on the magnetization so as to control the number of spin waves was further applied to antiferromagnets and ferrimagnets. Even frustrated antiferromagnets and random-bond ferromagnets were discussed within this renewed spin-wave scheme.

The ferrimagnetic modified spin-wave theory is particularly useful in illuminating both static and dynamic properties. One-dimensional ferrimagnets have lately attracted much attention especially in the context of designing molecule-based ferromagnets. Assembling molecular bricks in such a way as to obtain a low-dimensional system with a nonzero resultant spin in the ground state and then coupling the chains or the layers again in a ferromagnetic fashion, one can in principle obtain a molecular magnet. A series of bimetallic chain compounds were synthesized in such a strategy. Another approach to molecular magnets consists of bringing into interaction metal ions and stable organic radicals. Homometallic materials such as tetrameric bond-alternating chain compounds and trimeric intertwining double-chain compounds are distinct ferrimagnets of topological origin. Such synthetic endeavors have stimulated several experimentalists to measure $T_1$.

FIG. 1: Modified spin-wave calculations of the specific heat $C$ and the magnetic susceptibility $\chi$ as functions of temperature for the ferrimagnetic Heisenberg chains. The original (Takahashi) and our (Yamamoto) schemes are compared with quantum Monte Carlo (QMC) calculations.
on ferrimagnetic chain compounds. Thus motivated, we have started a modified spin-wave exploration\textsuperscript{22} of the nuclear spin dynamics in one-dimensional Heisenberg ferrimagnets beyond the conventional Raman mechanism. Here we give a full description of the theory and finally show a strong evidence of the proton spin relaxation in the ferrimagnetic chain compound NiCu\textsubscript{2}Cu\textsubscript{2}Cu\textsubscript{2}O\textsubscript{6} being mediated by the three-magnon scattering rather than the Raman one.

II. MODIFIED SPIN-WAVE SCHEME

We consider ferrimagnetic Heisenberg chains of alternating spins \( S \) and \( s \), as described by the Hamiltonian

\[
\mathcal{H} = \sum_{n=1}^{N} \left[ J \mathbf{S}_n \cdot (\mathbf{s}_{n-1} + \mathbf{s}_n) - (g_s \mathbf{S}_n^z + g_a \mathbf{s}_n^z) \mu_B H \right].
\]

Introducing bosonic operators for the spin deviation in each sublattice via \( S_i^+ = (2S - a_i^+ a_i)^{1/2} a_i \), \( S_i^z = S - a_i^z a_i \), \( s_i^+ = b_i^+ (2s - b_i^+ b_i)^{1/2} b_i \), \( s_i^z = -s + b_i^z b_i \), and assuming that \( O(S) = O(s) \), we expand the Hamiltonian with respect to \( 1/S \) as

\[
\mathcal{H} = -2SsJN + \mathcal{H}_1 + \mathcal{H}_0 + O(S^{-1}),
\]

where \( \mathcal{H}_1 \) contains the \( O(S') \) terms which are explicitly given in Appendix A.

Our scheme\textsuperscript{23} of modifying the spin-wave theory is distinct from the original idea proposed by Takahashi\textsuperscript{24} and Hirsch \textit{et al.}\textsuperscript{25} In their way of suppressing the divergence of the sublattice magnetizations, an effective Hamiltonian with a Lagrange multiplier included, instead of the original Hamiltonian, is diagonalized subject to zero staggered magnetization. On the other hand, we first diagonalize the Hamiltonian keeping the dispersion relations free from temperature and then introduce a Lagrange multiplier in order to minimize the free energy subject to zero staggered magnetization. The two approaches are compared in Fig. [1]. Our new scheme is much better at describing the antiferromagnetically peaked specific heat and the low-temperature diverging susceptibility. Our approach converges into the paramagnetic behavior at high temperatures for both the specific heat and susceptibility.

![Diagrammatic representation of various nuclear spin-lattice relaxation processes.](image)

FIG. 2: Diagrammatic representation of various nuclear spin-lattice relaxation processes. Solid arrows, designating spin waves which are emitted in the first-order processes, induce a nuclear spin flip (\( \times \)) via the hyperfine interaction, while broken arrows, depicting the four-magnon exchange correlations, thermally scatter the first-order spin waves as \textit{virtual excitations}, where spin waves of ferromagnetic and antiferromagnetic aspect are distinguishably drawn by straight and wavy arrows, respectively. (a) The first-order direct (single-magnon) relaxation processes; (b) The first-order Raman (two-magnon) relaxation processes; (c) The first-order and second-order three-magnon relaxation processes, where \( q = -k \), are related to each other through nonlinear equations and are therefore inseparable. Considering the nuclear-electronic energy conservation, processes in solid and dotted frames are of great and little significance, respectively, whereas those in broken frames are relevant according to the constituent spins \( S \) and \( s \). Labels \( W_{ss}^{ss} \) and \( W_{ss}^{ss'} \) on feasible processes are explained in Appendix A.
III. NUCLEAR SPIN-LATTICE RELAXATION

The hyperfine interaction is generally expressed as

$$\mathcal{H}_{\text{hf}} = g_s \mu_B \hbar \gamma N I^+ \sum_n \left( \frac{1}{2} A^+_n S^+_n + A^+_n \right) + g_s \mu_B \hbar \gamma N I^+ \sum_n \left( \frac{1}{2} B^-_n S^-_n + B^-_n \right),$$

(3.1)

where $A^+_n (B^-_n)$ is the dipolar coupling tensor between the nuclear and $n$th larger (smaller) electronic spins. Since $\mathcal{H}_0$ and $\mathcal{H}_{\text{hf}}$ are both much smaller than $\mathcal{H}_1$, they act as perturbative interactions to the linear spin-wave system. If we consider up to the second-order perturbation with respect to $\mathcal{V} \equiv \mathcal{H}_0 + \mathcal{H}_{\text{hf}}$, the probability of a nuclear spin being scattered from the state of $I^z = m$ to that of $I^z = m + 1$ is given by

$$W = \frac{2\pi}{h} \sum_{i} \left| \langle f | \mathcal{V} + \sum_{m(\neq i)} \mathcal{V}[m] | m \rangle \right|^2 \delta(E_i - E_f),$$

(3.2)

where $i$ and $f$ designate the initial and final states of the unperturbed electronic-nuclear spin system, whose energies are $E_i$ and $E_f$, respectively. The nuclear spin-lattice relaxation time is then given by $T_1 = (I - m)(I + m + 1)/2W$.

Equation (3.2) contains various scattering processes, which are diagrammatically shown in Fig. 2. Due to the considerable difference between the nuclear and electronic energy scales, $\hbar \omega_N \ll J$, the direct process, involving a single spin wave, is rarely of significance. Considering further that the antiferromagnetic spin waves are higher in energy than the ferromagnetic ones, $\omega^+_{k} < \omega^-_{k}$, at moderate fields, the intraband spin-wave scattering dominates the Raman relaxation rate $1/T^{(2)}_1$, whereas both the intraband and interband spin-wave scatterings contribute to the three-magnon relaxation rate $1/T^{(3)}_1$.

Within the first-order mechanism, $1/T^{(3)}_1$ is much smaller than $1/T^{(2)}_1$. However, the first-order relaxation rate may be enhanced through the second-order mechanism. We consider the leading second-order relaxation, that is, the exchange-scattering-induced three-magnon processes, as well as the first-order ones. The second-order Raman processes, containing two virtual magnons, are much more accidental due to the momentum conservation and much less contributive due to the $(4S)^{-1}$-damping factor in the Holstein-Primakoff magnon series expansion. As for the four-magnon scattering, the first-order processes are nonexistent, whereas the second-order ones originate in the six-magnon exchange interaction and therefore contain two virtual magnons. Thus and thus, all other higher-order processes do not significantly change the relaxation scenario. We explicitly formulate $1/T^{(2)}_1$ and $1/T^{(3)}_1$ in Appendix B.

IV. THREE-MAGNON VERSUS RAMAN PROCESSES

We calculate the cases of $(S, s) = (1, \frac{1}{2})$ and $(S, s) = (\frac{3}{2}, \frac{1}{2})$, which are relevant to several major materials. Figure 3 shows $1/T_1$ as a function of temperature and an applied field. The exchange-scattering-enhanced three-magnon relaxation rate generally grows into a major contribution to $1/T_1$ with increasing temperature and decreasing field. As temperature increases, $\bar{n}_N$ decreases at $k \approx 0$ but otherwise increases. In one dimension, excitations at $k \approx 0$ predominate in the Raman processes, while all the excitations are effective in the three-magnon processes. $1/T^{(2)}_1$ and $1/T^{(3)}_1$ are hence decreasing and increasing functions of temperature, respectively, unless temperature is so high as to activate the antiferromagnetic spin waves. The field dependences of $1/T^{(2)}_1$ and $1/T^{(3)}_1$ are also in striking contrast. At moderately low temperatures and weak fields, $\hbar \omega_N \ll k_B T \ll J$, $T^{(2)}_1$ is approximately evaluated as

$$\frac{1}{T^{(2)}_1} \approx \frac{2 \times (g_s A^2 S - g_s B^2 s) \mu_B \hbar \gamma N}{\pi \hbar S s (S - s) J} \times \exp \left( - \frac{(g_s + g_s) \mu_B H}{2k_B T} \right) K_0 \left( \frac{\hbar \omega_N}{2k_B T} \right),$$

(4.1)

where $K_0$ is the modified Bessel function of the second kind and behaves as $K_0(\hbar \omega_N/2k_B T) \approx 0.80908 - \ln(\hbar \omega_N/k_B T)$. Thus the field dependence of $1/T^{(2)}_1$ is initially logarithmic and then turns exponential with increasing field. Equation (B2) is much less analytical but suggests much stronger power-law diverging behavior with decreasing field. Therefore, the three-magnon relaxation predominates over the Raman one at weak fields.

In Fig. 4 we plot the crossover points on which $1/T^{(2)}_1 = 1/T^{(3)}_1$. A Raman-to-three-magnon crossover may generally be detected with increasing temperature and decreasing field. The ferrimagnetic nuclear spin-lattice relaxation is sensitive to another adjustable parameter $A^*/B^*$, that is, the location of the probe nuclei. At the special location of $A^*/B^* \approx (ds/ds)^3 \approx (S/s)^\sigma$, where $ds$ ($d_s$) is the distance between the nuclear and larger (smaller) electronic spins, the $\sigma$ excitation mode is almost invisible to the nuclear spin. In the case of $(S, s) = (1, \frac{1}{2})$, for example, the nuclear spin located as $A^*/B^* \approx 1/2$ hardly relaxes. Any $T_1$ measurements should be performed away from such magic points.

V. INTERPRETATION OF EXPERIMENTS

We are further excited to compare our theory with recent experimental findings. Fujiwara and Hagihara measured $T_1$ for proton nuclei in the bimetallic chain compound NiCu(pba)(H₂O)₃, 2H₂O (pba = 1, 3-propylenebis(oxamato) = C₂H₂O₅N₂O₆) comprising...
ferrimagnetic chains with alternating octahedral Ni$^{2+}$ and square-pyramidal Cu$^{2+}$ ions bridged by oxamato groups. The measured susceptibility is well reproduced with $g_S = 2.22$, $g_\tau = 2.09$ and $J/k_B \approx 121$ K. Since the protons relevant to the $T_1$ findings are located in close vicinity to Cu ions, we may set the coupling constants for $A'/B' = 0$. We further assume that $B^2 = 1.37 \times 10^{-20}$ $T^2/J$ and $(B^-/B^-)^2 = 4$, which can be consistent with the crystalline structure\cite{36}.

The thus-calculated $1/T_1$ is compared with the observations in Fig. 5. Considering that there may be larger uncertainty in the experimental analysis at lower temperatures\cite{31}, the theoretical and experimental findings are in good agreement and the slight discrepancy between them may be attributable, for instance, to weak momentum dependence of $B'_k$ and the protons of wide distribution. Figure 5(b) shows that the increasing behavior of $1/T_1$ at high temperatures originates from the three-magnon contribution. Figure 5(c) more impressively demonstrates the relevance of the three-magnon scattering to the proton spin relaxation. The strong field dependence can never be explained by the Raman process.

Since $1/T_1$ within the first-order mechanism stays much smaller than the observations, the exchange-scattering-induced three-magnon process is essential in interpreting such accelerated relaxation. We are eager to have reliable observations at lower temperatures and weaker fields. More extensive NMR measurements on the related compounds are encouraged.

VI. SUMMARY

There exist pioneering $T_1$ measurements on the layered ferrimagnet CrCl$_3$\cite{38} and the coupled-chain antiferromagnet CsMnCl$_3$·2H$_2$O\cite{39} which give evidence of the relevant three-magnon scattering. However, they are both, in some sense, classical findings under the existing three-dimensional long-range order. No author has explored one-dimensional quantum ferrimagnetic dynamics with particular interest in multi-magnon scattering beyond the Raman mechanism. We have reported the first evidence of the three-magnon scattering dominating one-dimensional nuclear spin relaxation. We hope the present research will stimulate further measurements and lead to close collaboration between theoretical and experimental investigations.

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FIG. 5: Proton spin relaxation-time measurements on NiCu(pba)(H\(_2\)O)\(_3\)-2H\(_2\)O (Ref. 34) compared with our theory. (a) 1/T\(_1\) as a function of temperature at various values of an applied field; (b) 1/T\(_1\) as a function of temperature at 3.15 T; (c) 1/T\(_1\) as a function of an applied field at 280 K. In (b) and (c), the Raman (1/T\(_1\)\(_{R}^{(2)}\)) and three-magnon (1/T\(_1\)\(_{3-magnon}^{(3)}\)) contributions are also plotted by dotted and broken lines, respectively.

APPENDIX A: SPIN-WAVE HAMILTONIAN

Performing the Fourier and then Bogoliubov transformations as \(N^{-1/2}\sum_n e^{i\mathbf{k} \cdot \mathbf{r}_n} a_n^\dagger = \alpha_k \text{ch} \theta_k - \beta_k \text{sh} \theta_k\) and \(N^{-1/2}\sum_n e^{-i\mathbf{k} \cdot \mathbf{r}_n} b_n^\dagger = \beta_k \text{ch} \theta_k - \alpha_k \text{sh} \theta_k\), where we abbreviate \(\text{ch} \theta_k\) and \(\text{sh} \theta_k\) as \(\text{ch} \theta_k\) and \(\text{sh} \theta_k\), respectively, the Hamiltonian is represented as

\[
\mathcal{H}_1 = -2JN[2\sqrt{S}S - (S + s)A] + \sum_k \left[\omega_1(k)\alpha_k^\dagger \alpha_k + \omega_1(k)\beta_k^\dagger \beta_k + \gamma_1(k)(\alpha_k^\dagger \beta_k^\dagger + \alpha_k^\dagger \beta_k)\right],
\]

\[
\mathcal{H}_0 = -2JN\left[A^2 + 2A - \left(\sqrt{\frac{S}{s}} + \sqrt{\frac{s}{S}}\right)\Gamma A\right] + \sum_k \left[\omega_0(k)\alpha_k^\dagger \alpha_k + \omega_0(k)\beta_k^\dagger \beta_k + \gamma_1(k)(\alpha_k^\dagger \beta_k^\dagger + \alpha_k^\dagger \beta_k)\right]
\]

\[
-\frac{J}{4N} \sum_{k_1,...,k_4} \delta(k_1 - k_2 - k_3 + k_4) \left[V_0^{(1)}(k_1, k_2, k_3, k_4)\alpha_{k_1}^\dagger \alpha_{k_2} \alpha_{k_3} \alpha_{k_4} + V_0^{(2)}(k_1, k_2, k_3, k_4)\beta_{k_1}^\dagger \beta_{k_2} \beta_{k_3} \beta_{k_4}ight]
\]

\[
+V_0^{(3)}(k_1, k_2, k_3, k_4)\alpha_{k_1}^\dagger \beta_{k_2} \beta_{k_3} \alpha_{k_4} + V_0^{(4)}(k_1, k_2, k_3, k_4)\beta_{k_1}^\dagger \beta_{k_2} \beta_{k_3} \beta_{k_4} + V_0^{(5)}(k_1, k_2, k_3, k_4)(\beta_{k_1}^\dagger \beta_{k_2} \beta_{k_3} \alpha_{k_4} + \text{H.c.}) + V_0^{(6)}(k_1, k_2, k_3, k_4)(\beta_{k_1} \alpha_{k_2} \beta_{k_3} \alpha_{k_4} + \text{H.c.})\right],
\]

where

\[
\Gamma = \frac{1}{2N} \sum_k \cos \frac{k}{2} \text{sh} 2\theta_k, \quad A = \frac{1}{2N} \sum_k (\text{ch} 2\theta_k - 1),
\]

\[
\omega_1^+(k) = (S + s + \frac{(gs-g_s)\mu_B H}{2J})\text{ch} \theta_k - 2\sqrt{S}\cos \frac{k}{2} \text{sh} 2\theta_k \pm (S + s - \frac{(gs-g_s)\mu_B H}{2J}),
\]

\[
\omega_1^-(k) = (S + s + \frac{(gs-g_s)\mu_B H}{2J})\text{ch} \theta_k - 2\sqrt{S}\cos \frac{k}{2} \text{sh} 2\theta_k \pm (S + s - \frac{(gs-g_s)\mu_B H}{2J}),
\]

\[
\gamma_1(k) = 2\sqrt{S}\cos \frac{k}{2} \text{ch} \theta_k - \left[\left(\frac{g_s}{2} + \frac{g_s}{2}\right)S - 2\Lambda\right] \frac{\text{ch} \theta_k}{2}\pm \frac{\text{sh} \theta_k}{2}
\]

\[
\gamma_0(k) = \left[2\Gamma - \sqrt{\left(\frac{S}{s} + \frac{s}{S}\right) A}\right] \cos \frac{k}{2} \text{ch} \theta_k + \left[2\Lambda - \sqrt{\left(\frac{S}{s} + \frac{s}{S}\right) A}\right] \text{sh} \theta_k,
\]

\[
V_0^{(1)}(k_1, k_2, k_3, k_4) = \left(\cos \frac{k_1-k_2}{2} + \cos \frac{k_3-k_4}{2}\right) (\text{ch} \theta_{k_1} \text{ch} \theta_{k_2} \text{sh} \theta_{k_3} \text{sh} \theta_{k_4} + \text{sh} \theta_{k_1} \text{ch} \theta_{k_2} \text{sh} \theta_{k_3} \text{ch} \theta_{k_4})
\]

\[
+ \left(\cos \frac{k_1-k_3}{2} + \cos \frac{k_2-k_4}{2}\right) (\text{ch} \theta_{k_1} \text{ch} \theta_{k_2} \text{sh} \theta_{k_3} \text{sh} \theta_{k_4} + \text{sh} \theta_{k_1} \text{ch} \theta_{k_2} \text{sh} \theta_{k_3} \text{ch} \theta_{k_4})
\]

\[
- \sqrt{\frac{S}{s}} \left[\text{sh} \theta_{k_1} \text{sh} \theta_{k_4} (\cos \frac{k_1}{2} \text{ch} \theta_{k_1} \text{sh} \theta_{k_2} + \cos \frac{k_2}{2} \text{sh} \theta_{k_1} \text{ch} \theta_{k_2} ) + \text{sh} \theta_{k_1} \text{sh} \theta_{k_2} (\cos \frac{k_3}{2} \text{ch} \theta_{k_3} \text{sh} \theta_{k_4} + \cos \frac{k_4}{2} \text{sh} \theta_{k_1} \text{ch} \theta_{k_4} )\right]
\]
\[V_0^{(2)}(k_1, k_2, k_3, k_4) = \left( \cos \frac{k_4 - k_3}{2} + \cos \frac{k_2 - k_1}{2} \right) (\text{ch}\theta_{k_1}\text{ch}\theta_{k_2}\text{ch}\theta_{k_3}\theta_{k_4} + \text{sh}\theta_{k_1}\theta_{k_2}\text{sh}\theta_{k_3}\text{sh}\theta_{k_4}) \]

\[V_0^{(3)}(k_1, k_2, k_3, k_4) = \left( \cos \frac{k_4 - k_3}{2} + \cos \frac{k_2 - k_1}{2} \right) (\text{ch}\theta_{k_1}\text{ch}\theta_{k_2}\theta_{k_3}\text{ch}\theta_{k_4} + \text{sh}\theta_{k_1}\text{sh}\theta_{k_2}\text{sh}\theta_{k_3}\text{sh}\theta_{k_4}) \]

\[V_0^{(4)}(k_1, k_2, k_3, k_4) = \left( \cos \frac{k_4 - k_3}{2} + \cos \frac{k_2 - k_1}{2} \right) (\text{ch}\theta_{k_1}\text{ch}\theta_{k_2}\text{sh}\theta_{k_3}\text{ch}\theta_{k_4} + \text{sh}\theta_{k_1}\text{ch}\theta_{k_2}\text{sh}\theta_{k_3}\text{sh}\theta_{k_4}) \]

\[V_0^{(5)}(k_1, k_2, k_3, k_4) = \left( \cos \frac{k_4 - k_3}{2} + \cos \frac{k_2 - k_1}{2} \right) (\text{ch}\theta_{k_1}\text{sh}\theta_{k_2}\text{ch}\theta_{k_3}\text{ch}\theta_{k_4} + \text{sh}\theta_{k_1}\text{ch}\theta_{k_2}\text{sh}\theta_{k_3}\text{sh}\theta_{k_4}) \]

\[V_0^{(6)}(k_1, k_2, k_3, k_4) = \left( \cos \frac{k_4 - k_3}{2} + \cos \frac{k_2 - k_1}{2} \right) (\text{ch}\theta_{k_1}\text{sh}\theta_{k_2}\text{sh}\theta_{k_3}\text{ch}\theta_{k_4} + \text{sh}\theta_{k_1}\text{ch}\theta_{k_2}\text{sh}\theta_{k_3}\text{sh}\theta_{k_4}) \]

\[\theta_k\text{ is determined so as to diagonalize the linear spin-wave Hamiltonian } H, \text{ that is, to satisfy } \gamma_\text{eff}(k) = 0. \quad \alpha_k^\dagger (\beta_k^\dagger) \text{ creates spin waves of ferromagnetic (antiferromagnetic) aspect.}^{32,33,34} \text{ Minimizing the free energy under the effective condition of zero staggered magnetization,}^{30} \text{ we obtain the optimum distribution functions as} \]

\[\langle \alpha_k^\dagger \alpha_k \rangle \equiv \bar{n}_k^\tau, \quad \langle \beta_k^\dagger \beta_k \rangle \equiv \bar{n}_k^\tau; \quad \bar{n}_k^\tau = \frac{1}{e^{(J\omega_\text{eff}(k) - \mu_\text{c} \text{ch}\theta_k)/k_BT} - 1}, \]

where \(\mu\) is determined through

\[\sum_k \sum_\omega S + s + (g_s - g_a)\mu B H/2J \omega_k \bar{n}_k^\tau = (S + s) N e^{-J\omega_\text{eff}(0)/k_BT}. \]
APPENDIX B: MAGNON SERIES EXPANSION OF THE RELAXATION RATE

Considering the significant difference between the nuclear and electronic energy scales and assuming the Fourier components of the coupling constants to have little momentum dependence as $\sum_n e^{i k n} A_n^\tau \equiv A_k^\tau \simeq A^\tau$ and $\sum_n e^{i k n} B_n^\tau \equiv B_k^\tau \simeq B^\tau \,(\tau = -, z)$, we obtain the Raman and three-magnon relaxation rates as

$$
\frac{1}{T_2^{(z)}} \simeq \frac{2(g_{\mu B}^\gamma \gamma N z)^2}{\hbar J N} \sum_{k, \sigma=\pm} \sum_{\tau=\pm} W^{\sigma\sigma}(\tau k_2^\sigma, k_1) n_{k_1}^\sigma (n_{k_2}^\sigma + 1) \left| \frac{d \omega^\sigma(k)}{dk} \right|^{-1} \, k = k_2^\sigma,
\tag{B1}
$$

$$
\frac{1}{T_1^{(z)}} \simeq \frac{(g_{\mu B}^\gamma \gamma N z)^2}{16 \hbar S J N^2} \sum_{k_1, k_2, k_3, \sigma=\pm} \sum_{\tau=\pm} 2 W^{\sigma\sigma}(\tau k_3^\sigma, k_1, k_2) n_{k_1}^\sigma n_{k_2}^\sigma (n_{k_3}^\sigma + 1) \left| \frac{d \omega^\sigma(k)}{dk} \right|^{-1} \, k = k_3^\sigma
$$

$$
+ W^{\bar{\sigma}\bar{\sigma}}(k_1, k_2, \tau k_3^\sigma, k_1) n_{k_1}^\bar{\sigma} n_{k_3}^\bar{\sigma} (n_{k_3}^\sigma + 1) \left| \frac{d \omega^\sigma(k)}{dk} \right|^{-1} \, k = k_3^\sigma,
\tag{B2}
$$

with $\bar{\sigma} = -\sigma$, where $k_2^\sigma$ and $k_3^\sigma$ are determined through $\omega_{k_1}^\sigma - \omega_{k_2^\sigma} + \hbar \omega_N / J = 0$ and $\omega_{k_1}^\sigma + \omega_{k_2^\sigma} - \omega_{k_3^\sigma} + \sigma' \hbar \omega_N / J = 0$, respectively, and

$$
W^{--}(k_1, k_2) = \frac{A^z}{B^z} \chi_{k_1} \chi_{k_2} - s h \theta_{k_1} s h \theta_{k_2}, \quad W^{++}(k_1, k_2) = \frac{A^z}{B^z} s h \theta_{k_1} s h \theta_{k_2} - s h \theta_{k_1} s h \theta_{k_2},
\tag{B3}
$$

$$
W^{--}(k_1, k_2, k_3) = \frac{A^z}{B^z} \chi_{k_1} \chi_{k_2} \chi_{k_3} - \frac{s}{s} \chi_{k_1} \chi_{k_2} \chi_{k_3} - 2 S V_0^{(1)}(k_1, k_2, k_3, k_3 + k_2 - k_1) \left| \frac{d \omega^\sigma(k)}{dk} \right|^{-1} \, k = k_3^\sigma,
\tag{B4}
$$

$$
W^{++}(k_1, k_2, k_3) = \frac{A^z}{B^z} \chi_{k_1} \chi_{k_2} \chi_{k_3} - \frac{s}{s} \chi_{k_1} \chi_{k_2} \chi_{k_3} - 2 S V_0^{(1)}(k_1, k_2, k_3, k_3 + k_2 - k_1) \left| \frac{d \omega^\sigma(k)}{dk} \right|^{-1} \, k = k_3^\sigma.
\tag{B4}
$$

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