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Low-temperature thermodynamics of one-dimensional alternating-spin Heisenberg ferromagnets

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Motivated by a novel bimetallic chain compound in which alternating magnetic centers are ferromagnetically coupled, we investigate thermodynamic properties of one-dimensional spin- (S, s) Heisenberg ferromagnets both numerically and analytically. On the one hand, quantum Monte Carlo calculations illuminate the overall thermal behavior. The specific heat may exhibit a double-peaked structure at intermediate temperatures for $S \geq 3s$ in general. On the other hand, a modified spin-wave theory precisely describes the low-temperature properties. Expanding the specific heat and the magnetic susceptibility, we reveal an analogy and a contrast between mixed-spin ferromagnets and ferrimagnets.

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I. INTRODUCTION

Much effort has been devoted to designing molecular systems ordering ferromagnetically.¹ One possible approach consists of assembling molecular bricks so 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. Numerous heterospin chain compounds have been synthesized along this line. Gleizes and Verdagner² made an attempt to alternate two types of metal ion along one crystallographic axis with antiferromagnetic intrachain interaction and obtained a pioneering example of quasi-one-dimensional ferrimagnets, of formula $\text{MnACu}(\text{dto})_2(\text{H}_2\text{O})_3 \cdot 4.5\text{H}_2\text{O}$ ($A = \text{Ni}, \text{Cu}$; $\text{dto} = \text{dithiooxalato} = \text{S}_2\text{C}_2\text{O}_2$). Kahn *et al.*³ synthesized another series of bimetallic chain compounds $\text{ACu}(\text{pbaOH}) \times (\text{H}_2\text{O})_3 \cdot n\text{H}_2\text{O}$ [$A = \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$; $\text{pbaOH} = 2\text{-hydroxys-1,3-propylenebis(oxamato)} = \text{C}_7\text{H}_6\text{N}_2\text{O}_7$], one of which indeed attained the three-dimensional ferromagnetic order at low temperatures.⁴ Caneschi *et al.*⁵ took an alternative strategy of bringing into interaction metal ions and stable organic radicals. This idea was developed toward polymeric chain compounds.⁶ The wide variety of chemical explorations stimulated the physical interest in mixed-spin chains.⁷⁻¹⁵

Most of the thus-far synthesized heterospin systems are characterized as ferrimagnets. Ferromagnetic intrachain coupling is observed in few cases. In such circumstances, $\text{MnNi}(\text{NO}_2)_4(\text{en})_2$ ($\text{en} = \text{ethylenediamine} = \text{C}_2\text{H}_8\text{N}_2$),¹⁶ proved to be a quasi-one-dimensional mixed-spin ferromagnet¹⁷ and caused renewed interest in mixed-spin chains. Gillon *et al.*¹⁸ calculated the spin density distribution by means of the density functional theory and quantitatively visualized the ferromagnetic nature of the $\text{Mn}(\text{II})$ - $\text{Ni}(\text{II})$ interaction. Fukushima *et al.*¹⁹ performed high-temperature series expansion of the thermal quantities and argued the magnetic structure including single-ion anisotropy and interchain exchange coupling. Now an increasing number of chemists and physicists are taking interest in heterospin ferromagnets.^{20,21}

Alternating-spin chains possess elementary excitations of dual aspect. In the case of antiferromagnetic coupling, the acoustic excitations reduce the ground-state magnetization and are thus of ferromagnetic nature, while the optical exci-

tations enhance the ground-state magnetization and are thus of antiferromagnetic nature. In the case of ferromagnetic coupling, on the other hand, both excitations are of ferromagnetic character. Therefore, the Schottky-type peak of the specific heat and the minimum of the susceptibility-temperature product, which are both ferrimagnetic features,^{10,22} are absent from mixed-spin ferromagnets. Nevertheless, mixed-spin ferromagnets and ferrimagnets behave similarly at low temperatures, which is the goal of this paper. Employing the world-line quantum Monte Carlo method²³ and a modified spin-wave theory,²⁴ we investigate thermodynamics of one-dimensional alternating-spin Heisenberg ferromagnets with particular emphasis on the intrinsic low-temperature properties.

II. MODIFIED SPIN-WAVE SCHEME

We consider two kinds of spins S and s ($S > s$) alternating on a ring with ferromagnetic exchange coupling ($J > 0$) between nearest neighbors, as described by the Hamiltonian

$$\mathcal{H} = -J \sum_{n=1}^N (\mathbf{S}_n \cdot \mathbf{s}_n + \mathbf{s}_n \cdot \mathbf{S}_{n+1}). \quad (2.1)$$

Even in one dimension, the conventional spin-wave theory²⁵⁻²⁷ gives a fine piece of information on the ground-state correlation.^{28,29} As for the thermal quantities, however, the low-temperature series expansion within the conventional scheme³⁰ only reproduces the leading term of the specific heat and nothing correct for the magnetic susceptibility.³¹ Then Takahashi³² modified the spin-wave formalism, imposing a constraint on the magnetization, and obtained an excellent description of the low-temperature thermodynamics of low-dimensional ferromagnets. We develop the modified scheme for mixed-spin ferromagnets.

In order to describe the spin deviation in each sublattice, bosonic operators are introduced as

$$S_n^+ = \sqrt{2S - a_n^\dagger a_n} a_n, \quad S_n^z = S - a_n^\dagger a_n,$$

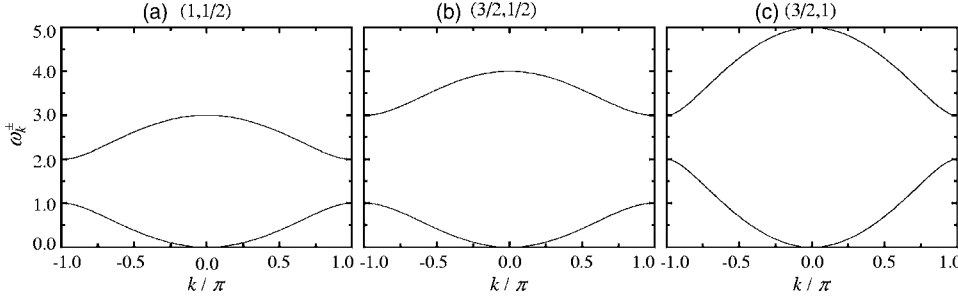


FIG. 1. Single-magnon excitation spectra as the rigorous dispersion relations of the elementary excitations for the spin- (S,s) ferromagnetic Heisenberg chains.

$$s_n^+ = \sqrt{2s - b_n^\dagger b_n} b_n, \quad s_n^- = s - b_n^\dagger b_n, \quad (2.2)$$

where we regard S and s as quantities of the same order. The bosonic Hamiltonian reads

$$\mathcal{H} = E_2 + \mathcal{H}_1 + \mathcal{H}_0 + O(S^{-1}), \quad (2.3)$$

where $E_2 = -2SsJN$ is the classical ground-state energy and \mathcal{H}_i is the $O(S^i)$ quantum correction to it. We consider first diagonalizing \mathcal{H}_1 and then taking \mathcal{H}_0 into calculation perturbationally.³³ Via the transformation

$$\begin{aligned} a_n^\dagger &= \frac{1}{\sqrt{N}} \sum_k e^{-ik(n-1/4)} (\alpha_k^\dagger \cos \theta_k - \beta_k^\dagger \sin \theta_k), \\ b_n^\dagger &= \frac{1}{\sqrt{N}} \sum_k e^{-ik(n+1/4)} (\alpha_k^\dagger \sin \theta_k + \beta_k^\dagger \cos \theta_k), \end{aligned} \quad (2.4)$$

with $\tan(2\theta_k) = 2\sqrt{Ss} \cos(k/2)/(S-s)$, we obtain

$$\mathcal{H}_1 = J \sum_k (\omega_k^- \alpha_k^\dagger \alpha_k + \omega_k^+ \beta_k^\dagger \beta_k). \quad (2.5)$$

Here the acoustic (ω_k^-) and optical (ω_k^+) dispersion relations are given by

$$\omega_k^\pm = S + s \pm \sqrt{(S-s)^2 + 4Ss \cos^2(k/2)} \equiv S + s \pm \omega_k, \quad (2.6)$$

and plotted in Fig. 1.

Now we proceed to the modified spin-wave scheme in an attempt to avoid thermal divergence of the number of bosons. At finite temperatures, we replace $\alpha_k^\dagger \alpha_k$ and $\beta_k^\dagger \beta_k$ by $\bar{n}_k^\mp \equiv \sum_{n^-, n^+} P_k(n^-, n^+) P_k(n^-, n^+)$, where $P_k(n^-, n^+)$ is the probability of n^- acoustic and n^+ optical spin waves appearing in the k -momentum state, and minimize the up-to- $O(S^1)$ free energy

$$\mathcal{F} = E_2 + J \sum_k \sum_{\sigma=\pm} \omega_k^\sigma \bar{n}_k^\sigma + k_B T \sum_k \sum_{n^-, n^+} P_k(n^-, n^+) \ln P_k(n^-, n^+), \quad (2.7)$$

with respect to $P_k(n^-, n^+)$'s under the condition of zero magnetization

$$(S+s)N - \sum_k \sum_{\sigma=\pm} \bar{n}_k^\sigma = 0, \quad (2.8)$$

together with the trivial constraints $\sum_{n^-, n^+} P_k(n^-, n^+) = 1$. Up to $O(S^1)$, the magnetic susceptibility and the internal energy at thermal equilibrium are expressed as

$$\chi = \frac{(g\mu_B)^2}{3k_B T} \sum_k \sum_{\sigma=\pm} \bar{n}_k^\sigma (\bar{n}_k^\sigma + 1), \quad (2.9)$$

$$E = E_2 + J \sum_k \sum_{\sigma=\pm} \omega_k^\sigma \bar{n}_k^\sigma, \quad (2.10)$$

with $\bar{n}_k^\pm = [e^{(J\omega_k^\pm - \mu)/k_B T} - 1]^{-1}$, where the g factors of the spins S and s are both set equal to g and the Lagrange multiplier μ is determined through the condition (2.8). The specific heat C is calculated by numerically differentiating the internal energy. The perturbational correction of $O(S^0)$ reads

$$\begin{aligned} \langle H_0 \rangle &\equiv \text{Tr}[\mathcal{H}_0 e^{-\mathcal{H}_1/k_B T}] / \text{Tr}[e^{-\mathcal{H}_1/k_B T}] \\ &= \frac{JN}{2} \left[\sqrt{\frac{S}{s}} (\Gamma_1 - \Gamma_2) \Gamma_3 + \sqrt{\frac{s}{S}} (\Gamma_1 + \Gamma_2) \Gamma_3 \right. \\ &\quad \left. - \Gamma_1^2 + \Gamma_2^2 - \Gamma_3^2 \right], \end{aligned} \quad (2.11)$$

with

$$\Gamma_1 = \frac{1}{N} \sum_k (\bar{n}_k^- + \bar{n}_k^+) = S + s,$$

$$\Gamma_2 = \frac{1}{N} \sum_k \frac{S-s}{\omega_k} (\bar{n}_k^- - \bar{n}_k^+),$$

$$\Gamma_3 = \frac{1}{N} \sum_k \frac{2\sqrt{Ss}}{\omega_k} \cos^2 \frac{k}{2} (\bar{n}_k^- - \bar{n}_k^+), \quad (2.12)$$

where we keep μ unchanged. Indeed μ may be modified so as to minimize the up-to- $O(S^0)$ free energy, but such a procedure, which is much more complicated, has no effect on the low-temperature leading behavior.³⁰ The thermal quantities are expanded in powers of $(k_B T/J)^{1/2}$ at low temperatures. The specific heat and the magnetic susceptibility start from $T^{1/2}$ and T^{-2} , respectively, and their leading three terms are not affected by the $O(S^0)$ interactions.

III. NUMERICAL RESULTS FOR THE OVERALL THERMAL BEHAVIOR

The world-line quantum Monte Carlo calculation is carried out at $N=24, 32, 40$ (48, 64, 80 spins) and is extrapolated to the $N \rightarrow \infty$ limit. However, any quantity divided by N does not vary with N beyond its statistical error in the temperature

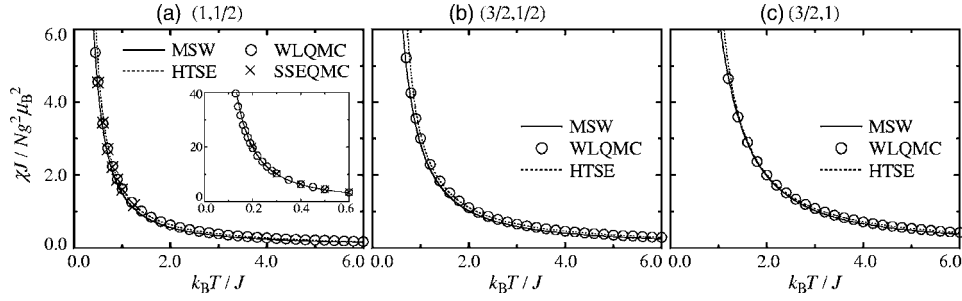


FIG. 2. The modified-spin-wave (MSW) and the world-line quantum Monte Carlo (WLQMC) calculations of the magnetic susceptibility χ as a function of temperature for the spin- (S,s) ferromagnetic Heisenberg chains. The numerical error is within the symbol size. High-temperature series-expansion (HTSE) and stochastic series-expansion quantum Monte Carlo (SSEQMC) calculations, which were performed up to $O[(J/k_B T)^7]$ and at $N=64$, respectively, by Fukushima *et al.* (Refs. 19 and 34), are also shown for reference. At $(S,s)=(1, \frac{1}{2})$, the low-temperature behavior is scaled up in an inset.

range to show. A few million Monte Carlo steps are spent on low-temperature calculations, while less than a half million steps on high-temperature calculations. The numerical precision in the final results is two to three digits.

In Fig. 2 we show the modified-spin-wave and the world-line quantum Monte Carlo calculations of the magnetic susceptibility together with preceding findings^{19,34} through the power series expansion of $e^{-\mathcal{H}/k_B T}$. Fukushima *et al.* pioneeringly applied a quantum Monte Carlo scheme combined with the stochastic series-expansion technique³⁵ to the mixed-spin ferromagnetic thermodynamics and further performed high-temperature series expansion for general S and s . The modified spin-wave calculations are in good agreement with numerical findings over the whole temperature range, reproducing the paramagnetic susceptibility $[S(S+1)+s(s+1)]N(g\mu_B)^2/3k_B T$ at high temperatures and revealing the T^{-2} -diverging behavior at low temperatures. The susceptibility-temperature product still monotonically decreases with increasing temperature in contrast with the ferromagnetic behavior.³⁶ The low-temperature behavior is later discussed in more detail.

In Fig. 3 we show the modified spin-wave and the world-line quantum Monte Carlo calculations of the specific heat together with preceding findings.^{19,34} The modified spin-wave calculations are less precise than those for the susceptibility but well reproduce the $T^{1/2}$ -initial behavior at low

temperatures and the spin-dependent peak structure at intermediate temperatures. The midtemperature structure of the specific heat may be regarded as a function of the acoustic excitation band width $W^- = 2sJ$ and the optical excitation gap $\Delta = 2SJ$ (see Fig. 1). The heat capacity attributable to the acoustic excitations and that to the optical excitations may be separable when $W^- \ll \Delta$. We find a single peak in Fig. 3(c) with $S/s=3/2$ but two humps in Fig. 3(b) with $S/s=3$. Further calculations for higher spins (Fig. 4) suggest that the peak stays single at $S/s=2$, while it splits in two at $S/s=4$. The intermediate temperature dependence is more featured with increasing S/s . We are empirically convinced that the double-peaked structure may appear for $S \geq 3s$, including practical cases $(S,s)=(\frac{5}{2}, \frac{1}{2}), (2, \frac{1}{2}), (\frac{3}{2}, \frac{1}{2})$. Mn(II)Cu(II), Fe(II)Cu(II), and Co(II)Cu(II) chain compounds³ have indeed been synthesized so far, but they all exhibit antiferromagnetic intrachain interaction. The double-peaked structure is much more pronounced for ferromagnetic intrachain interaction.^{19,34,37} We expect an increased effort to design ferromagnetic exchange coupling between alternating metal ions.

IV. ANALYTICAL RESULTS FOR THE LOW-TEMPERATURE BEHAVIOR

In order to elucidate the low-temperature thermal behavior, we define the state density function

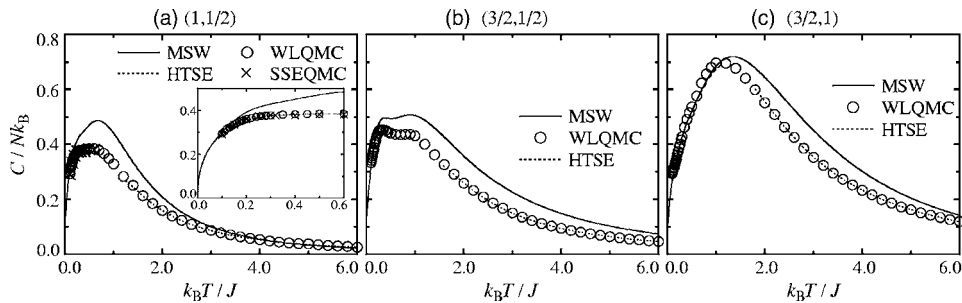


FIG. 3. The modified-spin-wave (MSW) and the world-line quantum Monte Carlo (WLQMC) calculations of the specific heat C as a function of temperature for the spin- (S,s) ferromagnetic Heisenberg chains. The numerical error is within the symbol size. High-temperature series-expansion (HTSE) and stochastic series-expansion quantum Monte Carlo (SSEQMC) calculations, which were performed up to $O[(J/k_B T)^{11}]$ and at $N=50$, respectively, by Fukushima *et al.* (Refs. 19 and 34), are also shown for reference. At $(S,s)=(1, \frac{1}{2})$, the low-temperature behavior is scaled up in an inset, where HTSE findings were elaborately obtained through a sophisticated Padé analysis (Ref. 19) of the series up to $O[(J/k_B T)^{29}]$.

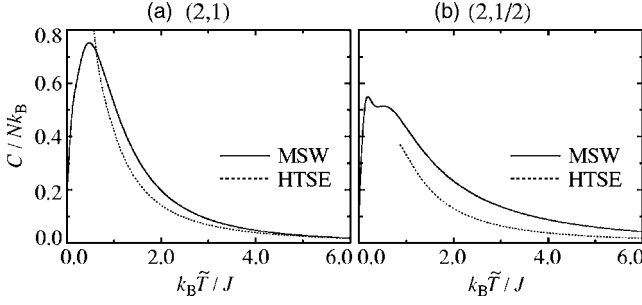


FIG. 4. The modified-spin-wave (MSW) calculations of the specific heat C as a function of temperature for the spin- (S, s) ferromagnetic Heisenberg chains in the cases of $S < 3s$ (a) and $S > 3s$ (b). High-temperature series-expansion (HTSE) calculations up to $O[(J/k_B T)^{11}]$ by Fukushima *et al.* (Ref. 19) are also shown for reference. The temperature scale is effectively enhanced with increasing S and s and therefore temperature is renormalized as $T/\sqrt{Ss(S+1)(s+1)} \equiv \tilde{T}$ (Ref. 19).

$$w^\pm(x) = \frac{1}{2\pi} \int_{-\pi}^{\pi} \delta(x - \omega_k^\pm) dk. \quad (4.1)$$

Here we are interested in the gapless acoustic branch and expand $w^-(x)$ for small x as

$$w^-(x) = \frac{1}{\pi} \sqrt{\frac{S+s}{2Ss}} \sum_{n=0}^{\infty} c_n^- x^n. \quad (4.2)$$

A few leading coefficients are given as

$$c_0^- = 1,$$

$$c_1^- = \frac{(S-s)^2 + Ss}{4Ss(S+s)},$$

$$c_2^- = \frac{(3S^2 - 4Ss + 3s^2)(S+s)^2 - 5S^2s^2}{32S^2s^2(S+s)^2}. \quad (4.3)$$

Applying Eq. (4.2) and neglecting the optical excitations \bar{n}_k^+ , Eq. (2.8) reads

$$v^{1/2} = \frac{1}{\pi\sqrt{2Ss(S+s)}} \sum_{n=0}^{\infty} c_n^- t^{n+1/2} \Gamma\left(n + \frac{1}{2}\right) \left[\Gamma\left(\frac{1}{2} - n\right) v^n + \sum_{m=0}^{\infty} \frac{(-1)^m}{m!} \zeta\left(n - m + \frac{1}{2}\right) v^{m+1/2} \right], \quad (4.4)$$

where $v = -\mu/k_B T$, $t = k_B T/J$, and $\zeta(n)$ is Riemann's zeta function. Solving this equation iteratively, we obtain the low-temperature expansion of the Lagrange multiplier as

$$v^{1/2} = \frac{c_0^- \Gamma(1/2)}{\pi\sqrt{2Ss(S+s)}} \Gamma\left(\frac{1}{2}\right) t^{1/2} + \left[\frac{c_0^- \Gamma(1/2)}{\pi\sqrt{2Ss(S+s)}} \right]^2 \Gamma\left(\frac{1}{2}\right) \zeta\left(\frac{1}{2}\right) t + \left[\frac{c_0^- \Gamma(1/2)}{\pi\sqrt{2Ss(S+s)}} \right]^3 \Gamma\left(\frac{1}{2}\right) \left[\zeta\left(\frac{1}{2}\right) \right]^2 t^{3/2} + O(t^2). \quad (4.5)$$

Since the magnetic susceptibility and the internal energy read

$$\frac{\chi k_B T}{N(g\mu_B)^2} = \frac{1}{3\pi} \sqrt{\frac{S+s}{2Ss}} \sum_{n=0}^{\infty} c_n^- t^{n+1/2} \Gamma\left(n + \frac{1}{2}\right) \left[\Gamma\left(\frac{3}{2} - n\right) v^{n-3/2} + \sum_{m=0}^{\infty} \frac{(-1)^m}{m!} \zeta\left(n - m - \frac{1}{2}\right) v^m \right], \quad (4.6)$$

$$\frac{E - E_2}{NJ} = \frac{1}{\pi} \sqrt{\frac{S+s}{2Ss}} \sum_{n=0}^{\infty} c_n^- t^{n+3/2} \Gamma\left(n + \frac{3}{2}\right) \left[\Gamma\left(-\frac{1}{2} - n\right) v^{n+1/2} + \sum_{m=0}^{\infty} \frac{(-1)^m}{m!} \zeta\left(n - m + \frac{3}{2}\right) v^m \right], \quad (4.7)$$

the susceptibility and the specific heat are expanded as

$$\frac{\chi J}{N(g\mu_B)^2} = \frac{1}{Ss} \left\{ \frac{\tilde{t}^{-2}}{3} - \frac{\zeta(1/2)}{\sqrt{2\pi}} \tilde{t}^{-3/2} + \left[\frac{\zeta(1/2)}{\sqrt{2\pi}} \right]^2 \tilde{t}^{-1} \right\} + O(\tilde{t}^{-1/2}), \quad (4.8)$$

$$\frac{C}{Nk_B} = (S+s) \left\{ \frac{3\zeta(3/2)}{4\sqrt{2\pi}} \tilde{t}^{1/2} - \tilde{t} + \frac{15[(S^2 - Ss + s^2)\zeta(5/2) - 4\zeta(1/2)]}{32\sqrt{2\pi}} \tilde{t}^{3/2} \right\} + O(\tilde{t}^2), \quad (4.9)$$

where $\tilde{t} = t/Ss(S+s) = k_B T/JSs(S+s)$. The $O(S^0)$ interactions affect the fourth and higher terms and therefore, whether through the Holstein-Primakoff transformation²⁶ or through the Dyson-Maleev transformation,^{27,38} we reach the same results (4.8) and (4.9).

Numerically solving the thermodynamic Bethe-ansatz integral equations for the spin- $\frac{1}{2}$ ferromagnetic Heisenberg chain, Takahashi and Yamada³¹ obtained

$$\frac{\chi J}{L(g\mu_B)^2} = 0.04167t^{-2} + 0.145t^{-3/2} + 0.17t^{-1} + O(t^{-1/2}), \quad (4.10)$$

$$\frac{C}{Lk_B} = 0.7815t^{1/2} - 2.00t + 3.5t^{3/2} + O(t^2), \quad (4.11)$$

where L is the number of spins. When we set S and s both equal to $\frac{1}{2}$, the expressions (4.8) and (4.10) coincide in their leading three terms, while Eqs. (4.9) and (4.11) in their leading two terms. The modified spin-wave calculations are thus

reliable and give rigorous information on the low-temperature properties. In the case of arbitrary S and s , the leading three terms of Eq. (4.8) and the leading two terms of Eq. (4.9) coincide with those of the spin- $[Ss(S+s)/2]^{1/3}$ uniform ferromagnetic chain except for a common factor. Considering practical combinations of S and s , we may estimate that $[Ss(S+s)/2]^{1/3} = [1 - (S-s)^2/(S+s)^2]^{1/3}(S+s)/2 \approx (S+s)/2$. Thus, ferromagnetically coupled alternating spins S and s look similar to a ferromagnetic assembly of virtual spins $(S+s)/2$ at low temperatures.

It is also interesting to compare the expressions (4.8) and (4.9) with those of ferrimagnetic chains.²⁴ It turns out that the spin- (S, s) ferrimagnetic low-temperature expansions are obtained by replacing J and s by $-J$ and $-s$, respectively, in Eqs. (4.8) and (4.9). In other words, antiferromagnetically coupled alternating spins S and s look like a ferromagnetic assembly of virtual spins $[Ss(S-s)/2]^{1/3} = [(S+s)^2/(S-s)^2 - 1]^{1/3}(S-s)/2$ at low temperatures. The quantity $[Ss(S-s)/2]^{1/3}$ is less intuitive than the corresponding $[Ss(S+s)/2]^{1/3}$ in the case of ferromagnetic coupling, but it results in a realistic spin quantum number $S-s$ when S is equal to $2s$. Equation (4.8) is nothing but the susceptibility of the spin- (S, s) ferrimagnetic chain if we set \tilde{t} for $k_B T / JSs(S-s)$ instead of $k_B T / JSs(S+s)$. All in all, the low-temperature physics is scaled by $S+s$ in ferromagnetic chains, whereas by $S-s$ in ferrimagnetic chains.

V. CONCLUDING REMARKS

Thermodynamic properties of alternating-spin Heisenberg ferromagnetic chains have been investigated in comparison with heterospin ferrimagnetic and homospin ferromagnetic chains. The magnetic susceptibility is a monotonically decreasing function of temperature regardless of (S, s) and is qualitatively the same as those of uniform ferromagnetic chains. The specific heat qualitatively varies with (S, s) and

exhibits a rich structure at intermediate temperatures. It may be double-peaked for $S \geq 3s$ in general.

The low-temperature behavior has been revealed analytically. The thermal quantities are still expanded in powers of $T^{1/2}$ and exhibit ferromagnetic features. The conventional spin-wave theory misunderstands the low-temperature behavior as series of T . The missing terms are reproduced through the modified procedure. Ferromagnetic and ferrimagnetic mixed-spin chains are qualitatively alike at low temperatures. The spin- (S, s) ferromagnetic chain looks similar to a ferromagnetic assembly of virtual spins $[Ss(S+s)/2]^{1/3} = [1 - (S-s)^2/(S+s)^2]^{1/3}(S+s)/2 \approx (S+s)/2$, while the spin- (S, s) ferrimagnetic chain behaves similar to that of virtual spins $[Ss(S-s)/2]^{1/3} = [(S+s)^2/(S-s)^2 - 1]^{1/3}(S-s)/2$. The present findings are really complementary to the sophisticated high-temperature series-expansion calculations.^{39,40}

The existent bimetallic chain ferromagnet $\text{MnNi}(\text{NO}_2)_4(\text{en})_2$ possesses a rather weak intrachain exchange coupling ($J/k_B \approx 2$ K), in which the low-temperature thermodynamics revealed here is hard to verify. Nevertheless such a pioneering material must highly motivate further explorations in both chemical and physical fields, as was the case with uniform ferromagnetic chains.^{30-32,41-43} In addition to bimetallic chain compounds, several authors⁴⁴ made a novel attempt to design low-dimensional heterospin systems utilizing organic triradicals. Mixed-spin chains contain further interesting topics such as dynamic structure factors of dual aspect⁴⁵ and nuclear spin relaxation through the exchange-scattering-enhanced three-magnon process.⁴⁶ We hope our study will stimulate further experimental investigations into mixed-spin chain compounds.

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