Low-energy structure of the homometallic intertwining double-chain ferrimagnets $A_3Cu_3(PO_4)_4$ (A=Ca,Sr,Pb)

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Motivated by the homometallic intertwining double-chain ferrimagnets $A_3Cu_3(PO_4)_4$ (A=Ca,Sr,Pb), we investigate the low-energy structure of their model Hamiltonian $\mathcal{H}=\Sigma_n[J_1(\boldsymbol{S}_{n:1}+\boldsymbol{S}_{n:3})+J_2(\boldsymbol{S}_{n+1:1}+\boldsymbol{S}_{n-1:3})]\cdot\boldsymbol{S}_{n:2}$, where $\boldsymbol{S}_{n:l}$ stands for the Cu^{2+} ion spin labeled l in the nth trimer unit, with particular emphasis on the range of bond alternation $0<J_2/J_1<1$. Although the spin-wave theory, whether up to $O(S^1)$ or up to $O(S^0)$, claims that there exists a flatband in the excitation spectrum regardless of bond alternation, a perturbational treatment, as well as the exact diagonalization of the Hamiltonian, reveals its weak but nonvanishing momentum dispersion unless $J_2=J_1$ or $J_2=0$. Quantum Monte Carlo calculations of the static structure factor further convince us of the low-lying excitation mechanism, elucidating similarities and differences between the present system and alternating-spin linear-chain ferrimagnets.

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I. INTRODUCTION

It is a long-standing and still challenging theme in materials science to design molecular systems of ferromagnetic order.[1] The naivest idea of ferromagnetically coupling nearest-neighbor magnetic centers leads to the highest spin multiplicity but critically depends on some structural parameters which are hard to handle chemically. An alternative solution to highly magnetic ground states consists of aligning molecular bricks so as to obtain a nonzero resultant spin in the ground state and then coupling the chains again in a ferromagnetic fashion. A variety of quasi-one-dimensional ferrimagnets were thus synthesized and not a few of them have been attracting theoretical, as well as experimental, interest.

Bimetallic chain compounds are early examples and among others is $MnCu(pbaOH)(H_2O)_3$ [pbaOH=2-hydroxy-1,3-propylenebis(oxamato)=$C_7H_6N_2O_7$],[2] which retains the long-range ferromagnetic order on the scale of the crystal lattice. Replacing the Mn^{2+} ions by Fe^{2+}, Co^{2+}, and Ni^{2+} ions, van Koningsbruggen *et al.* further synthesized a series of isomorphous compounds,[3] which stimulated extensive chemical explorations of heterometallic chain magnets[4,5] and systematic theoretical investigations of alternating-spin chains.[6–14] In an attempt to obtain substantially larger couplings between neighboring magnetic centers and possibly attain transitions to three-dimensional order at higher temperatures, Caneschi *et al.*[15] made a distinct attempt to bring into interaction metal ions and stable organic radicals. The representative materials of general formula $Mn(hfac)_2$NIT-R (hfac=hexafluoroacetylacetonate=$C_5H_2O_2F_6$; NIT-R=nitronyl nitroxide radical=$C_7H_{12}N_2O_2$-R with R=CH_3,C_2H_5,C_3H_5,C_6H_5) indeed exhibit antiferromagnetic intrachain interactions ranging from 200 to 330 cm^{-1}. The metal-radical hybrid strategy, combined with fabrication of novel polyradicals,[16] yielded various polymerized heterospin chain compounds.[17,18]

Homometallic ferrimagnetism is also realizable[19,20] but its mechanism is often more subtle, essentially depending on the structural features of the system. Coronado *et al.*[21,22] pioneeringly synthesized chain-structured compounds of such kind, $M_2(EDTA)(H_2O)_4\cdot 2H_2O$ (M=Ni,Co; EDTA=ethylenediamminetetraacetate=$C_{10}N_2O_8$), whose ferrimagnetic behavior originates from the alternating g factors and is therefore faint. Homometallic chain compounds of more pronouncedly ferrimagnetic aspect[23–26] were not obtained until another decade had passed, where particular topologies were elaborately imposed on the intrachain exchange interactions. A series of compounds, M(R-py)$_2$(N_3)$_2$ (M=Cu,Mn; R-py=pyridinic ligand=C_5H_4N-R with R=Cl,CH_3, etc.), consists of bond-polymerized homometallic chains, where the neighboring metal ion spins are bridged by versatile azido ligands and are coupled to each other ferromagnetically or antiferromagnetically.

The homometallic intertwining double-chain compounds $A_3Cu_3(PO_4)_4$ (A=Ca,Sr,Pb),[27–29] which are illustrated in Fig. 1, are topological ferrimagnets[30] in the strict sense. Their hybrid analogs $Ca_{3-x}Sr_xCu_3(PO_4)_4$ ($0\leqslant x\leqslant 3$) (Ref. 28) were also fabricated in an attempt to tune the antiferromagnetic bridges between the Cu(1) and Cu(2) sites, labeled J_1 and J_2, and possibly explore how paramagnetic spins grow into bulk ferrimagnets. The magnetic centers without single ion anisotropy and the simple crystalline structure without any organic ligand will contribute toward revealing intrinsic features of one-dimensional ferrimagnetic phenomena. Thus motivated, various experiments have been performed on these copper phosphates in recent years, including high-field magnetization,[31] specific-heat,[32] inelastic neutron-scattering,[33] nuclear spin-lattice relaxation-time,[34] and electron-spin-resonance[35] measurements.

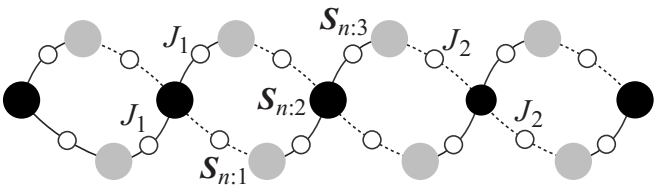

FIG. 1. Cu^{2+} trimeric chains in $A_3Cu_3(PO_4)_4$. The strongly coupled Cu^{2+} trimer consists of a central square planar Cu^{2+}(1) ion (black circle) and two pyramidal Cu^{2+}(2) ions (gray circles) bridged by oxygen ions (open circles).

It is therefore unfortunate that theoretical investigations of this system still stay in their early stage.[30,36,37] Indeed, there exists a field-theoretical study[38] deserving special mention, but the authors restricted their argument to the particular case of $J_1=J_2$, taking a main interest in realizing organic ferromagnetism. A recent numerical diagonalization study[39] is also a fine guide to this system, but the authors still devoted themselves to clarifying the electronic correlation effect on unsaturated ferromagnetism rather than geometrically modifying this unique bipartite lattice, starting from a model of the Hubbard type. An introduction of bond alternation $\delta \equiv J_2/J_1 \neq 1$ to this system will not only contribute toward understanding the magnetic properties of $A_3Cu_3(PO_4)_4$ (Refs. 28, 30, 33, and 34) but also illuminate the characteristic of the uniform point $\delta=1$. We are thus led to report the whole excitation mechanism of homogeneous-spin intertwining double-chain ferrimagnets, employing both analytical and numerical tools. According to the spin-wave theory, there exist three modes of elementary excitation, two of which exhibit parallel dispersion relations, while the rest of which is of no dispersion, regardless of bond alternation. However, the exact-diagonalization and perturbational calculations disprove the spin-wave scenario that the low-lying excitation spectrum remains qualitatively unchanged with varying δ. Indeed, there exist local excitations which are rigorously immobile at $\delta=1$, but *they can be itinerant with δ moving away from unity*. Except for the two particular points $\delta=1$ and $\delta=0$, corresponding to a plaquette chain and decoupled trimers, respectively, *there is no flatband in the excitation spectrum of the homogeneous-spin trimeric chain*. We further inquire into thermal excitations based on such an energy spectrum. Calculating the static structure factor as a function of temperature for an alternating-spin linear-chain ferrimagnet, as well as for the present system, we show what are the universal ferrimagnetic features and how they vary with decreasing δ.

II. PLAQUETTE CHAINS

The Hamiltonian of our interest is represented as

$$\mathcal{H} \equiv \mathcal{H}_1 + \mathcal{H}_2 = \sum_{n=1}^{N} [J_1(\boldsymbol{S}_{n:1} + \boldsymbol{S}_{n:3}) \cdot \boldsymbol{S}_{n:2} + J_2(\boldsymbol{S}_{n+1:1} + \boldsymbol{S}_{n-1:3}) \cdot \boldsymbol{S}_{n:2}], \tag{2.1}$$

where $\boldsymbol{S}_{n:l}$ symbolizes the Cu^{2+} ion spin $\left(S=\frac{1}{2}\right)$ labeled l in the nth trimer unit (see Fig. 1) and the intratrimer (J_1) and intertrimer (J_2) exchange interactions, denoted by $\mathcal{H}_1$ and $\mathcal{H}_2$, respectively, are defined as $0 \leqslant J_2 \leqslant J_1$. First, we take a look at the particular point of $J_2/J_1 \equiv \delta=1$, where the model reads a plaquette chain, bearing some analogy with a linear chain of alternating spins 1 and $\frac{1}{2}$.

Introducing bosonic operators through the Holstein-Primakoff transformation,

$$\begin{aligned} S^+_{n:1} &= \sqrt{2S - a^\dagger_{n:1}a_{n:1}}\,a_{n:1}, \quad S^z_{n:1} = S - a^\dagger_{n:1}a_{n:1}, \\ S^+_{n:2} &= a^\dagger_{n:2}\sqrt{2S - a^\dagger_{n:2}a_{n:2}}, \quad S^z_{n:2} = a^\dagger_{n:2}a_{n:2} - S, \\ S^+_{n:3} &= \sqrt{2S - a^\dagger_{n:3}a_{n:3}}\,a_{n:3}, \quad S^z_{n:3} = S - a^\dagger_{n:3}a_{n:3}, \end{aligned} \tag{2.2}$$

defining their Fourier transforms as

$$a_{k:l} = \frac{1}{\sqrt{N}} \sum_n e^{i(-1)^l k(n+l/2-1)} a_{n:l}, \tag{2.3}$$

with the lattice constant set equal to unity, and further processing them via the Bogoliubov transformation,

$$\begin{aligned} \alpha^\dagger_{k:-} &= \psi_{-1}(k)a^\dagger_{k:1} + \psi_{-2}(k)a_{k:2} + \psi_{-3}(k)a^\dagger_{k:3}, \\ \alpha^\dagger_{k:0} &= \psi_{01}(k)a^\dagger_{k:1} + \psi_{02}(k)a_{k:2} + \psi_{03}(k)a^\dagger_{k:3}, \\ \alpha^\dagger_{k:+} &= \psi_{+1}(k)a_{k:1} + \psi_{+2}(k)a^\dagger_{k:2} + \psi_{+3}(k)a_{k:3}, \end{aligned} \tag{2.4}$$

we reach a spin-wave Hamiltonian,

$$\mathcal{H} = E_g + \sum_{\lambda=\mp,0} \omega_\lambda(k)\alpha^\dagger_{k:\lambda}\alpha_{k:\lambda}, \tag{2.5}$$

with $E_g=\Sigma_{i=2,1,0}E_g^{(i)}$ and $\omega_\lambda(k)=\Sigma_{i=1,0}\omega_\lambda^{(i)}(k)$, where $E_g^{(2)}=-2S^2(J_1+J_2)N$ is the classical ground-state energy, while $E_g^{(i)}$ and $\omega_\lambda^{(i)}(k)$ $(i=1,0,\ldots)$ are the $O(S^i)$ quantum corrections to the ground-state energy and the dispersion relation of mode λ, respectively. Here, we have discarded the $O(S^{-1})$ terms. There are several ways[40–44] of treating the quartic interactions. When we diagonalize the one-body terms and then take account of the two-body terms perturbationally,[45] the spin-wave energies read

$$\frac{E_g^{(1)}}{J_1 N} = \frac{S(1+\delta)}{2N} \sum_k [\omega(k) - 3], \tag{2.6}$$

$$\frac{E_g^{(0)}}{J_1 N} = \frac{1+\delta}{2}(\Gamma^2 - 1) - \frac{2\delta}{1+\delta}(3\Gamma^2 + 2\Lambda^2 - 5\Gamma\Lambda - 3\Gamma + 3\Lambda), \tag{2.7}$$

$$\frac{\omega_\mp^{(1)}(k)}{J_1} = \frac{S(1+\delta)}{2}[\omega(k) \mp 1], \quad \frac{\omega_0^{(1)}(k)}{J_1} = S(1+\delta), \tag{2.8}$$

$$\begin{aligned} \frac{\omega_\mp^{(0)}(k)}{J_1} = \frac{1+\delta}{2}[\Gamma\Gamma(k) \mp \Gamma] - \frac{\delta}{1+\delta}[&6\Gamma\Gamma(k) - 5\Gamma\Lambda(k) \\ &- 5\Lambda\Gamma(k) + 4\Lambda\Lambda(k) - 3\Gamma(k) + 3\Lambda(k) \mp \Gamma \pm \Lambda], \end{aligned}$$

$$\frac{\omega_0^{(0)}(k)}{J_1} = -\frac{1+\delta}{2}(\Gamma - 1) - \frac{2\delta}{1+\delta}(\Gamma - \Lambda), \tag{2.9}$$

and their eigenvectors are given by

$$\psi_{\mp 1}(k) = \psi^*_{\mp 3}(k) = \frac{2(e^{\pm ik/2} + \delta e^{\mp ik/2})}{(1+\delta)\sqrt{2\omega(k)[3 \mp \omega(k)]}},$$

$$\psi_{\mp 2}(k) = \sqrt{\frac{3 \mp \omega(k)}{2\omega(k)}}, \quad \psi_{01}(k) = \frac{1}{\sqrt{2}},$$

$$\psi_{02}(k) = 0, \quad \psi_{03}(k) = -\frac{e^{-ik/2} + \delta e^{ik/2}}{\sqrt{2}(e^{ik/2} + \delta e^{-ik/2})}, \tag{2.10}$$

where

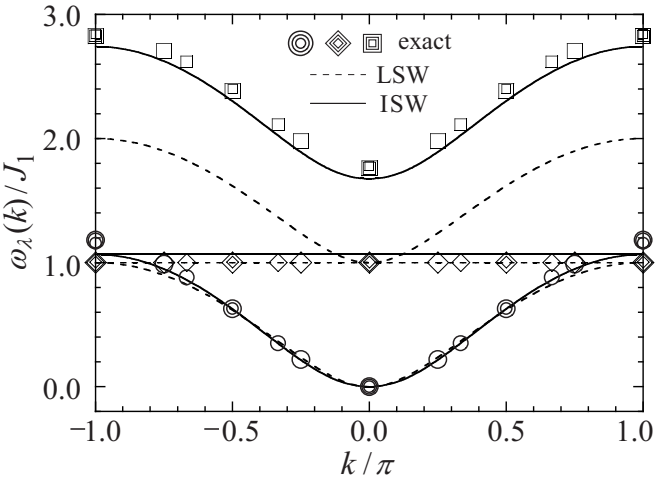

FIG. 2. Dispersion relations of the elementary excitations in the spin-$\frac{1}{2}$ plaquette chain, two (circles and diamonds) of which reduce the ground-state magnetization and are thus of ferromagnetic character, while the rest (squares) of which enhances the ground-state magnetization and is thus of antiferromagnetic character. The exact-diagonalization results at $N=4$, 6, and 8 are presented by symbols of small, middle, and large sizes, respectively, whereas the up to $O(S^1)$ linear (LSW) and up to $O(S^0)$ interacting (ISW) spin-wave calculations are given by the dotted and solid lines, respectively.

$$\omega(k) = \sqrt{1 + \frac{32\delta}{(1+\delta)^2}\sin^2\frac{k}{2}}, \tag{2.11}$$

$$\Gamma = \frac{1}{N}\sum_k \Gamma(k) = \frac{1}{N}\sum_k \frac{1}{\omega(k)},$$

$$\Lambda = \frac{1}{N}\sum_k \Lambda(k) = \frac{1}{N}\sum_k \frac{\cos k}{\omega(k)}. \tag{2.12}$$

Figure 2 shows the thus-calculated spin-wave excitation modes together with the exact eigenvalues. Free spin waves describe well the ferromagnetic modes $\omega_-(k)$ and $\omega_0(k)$, while higher-order quantum corrections play an essential role in reproducing the antiferromagnetic mode $\omega_+(k)$. The $O(S^0)$ quantum corrections significantly improve fully delocalized magnetic excitations in general,[18,41,46] but the standard Holstein-Primakoff magnon series expansion seems not to work well for highly localized excitations. The dispersive branches $\omega_\mp(k)$ are nothing but the elementary excitation modes of spin-alternating linear-chain Heisenberg ferrimagnets.[47] They are parallel within the spin-wave theory, but their difference $\omega_+(k)-\omega_-(k)$, is, in fact, momentum dependent. On the other hand, the flatband $\omega_0(k)$ arises from further excitation degrees of freedom in the present system. When $J_1=J_2$, Hamiltonian (2.1) reads

$$\mathcal{H} = J_1\sum_{n=1}^{N}(\boldsymbol{S}_{n:2}+\boldsymbol{S}_{n+1:2})\cdot\boldsymbol{T}_{n:3;n+1:1}, \tag{2.13}$$

with composite spins $\boldsymbol{T}_{n:3;n+1:1}\equiv\boldsymbol{S}_{n:3}+\boldsymbol{S}_{n+1:1}$, each lying diagonally across an elementary plaquette. Since Hamiltonian (2.13) commutes with $\boldsymbol{T}^2_{n:3;n+1:1}\equiv T_{n:3;n+1:1}(T_{n:3;n+1:1}+1)$, we have good quantum numbers $T_{n:3;n+1:1}$, each taking either 0 or 1. Therefore, the plaquette-chain Hamiltonian is block diagonalized by the set of numbers $\{T_{n:3;n+1:1}; n=1,2,\ldots,N\}$,[48] as well as by the total magnetization $\Sigma_{n=1}^{N}(S^z_{n:2}+T^z_{n:3;n+1:1})\equiv\mathcal{M}$. The Hilbert space of $\Sigma_{n=1}^{N}(\boldsymbol{T}_{n:3;n+1:1})^2/2=\Sigma_{n=1}^{N}(\boldsymbol{S}_{n:3}\cdot\boldsymbol{S}_{n+1:1}+3/4)\equiv\mathcal{N}=N$ corresponds to the ferrimagnetic chain of alternating spins 1 and $\frac{1}{2}$ and, consequently, we have here exactly the same dispersion relations[46] of elementary excitations. The Hilbert space of $\mathcal{N}=N-1$ and $\mathcal{M}=N/2-1$ consists of N subspaces labeled $\{T_{1:3;2:1},T_{2:3;3:1},\ldots,T_{N:3;1:1}\}=\{0,1,\ldots,1\},\{1,0,1,\ldots,1\},\ldots,\{1,\ldots,1,0\}$, and they all give the same set of eigenvalues, forming N flatbands. We find the lowest one in Fig. 2.

Thus, the spin-S plaquette chain turns out a combination of the alternating-spin-$(2S,S)$ linear chain and extra excitation degrees of freedom within the composite spins $\boldsymbol{T}_{n:3;n+1:1}$. All the composite spins are saturated in the ground state, $\boldsymbol{T}^2_{n:3;n+1:1}=2S(2S+1)$, and therefore, their excitations are necessarily of ferromagnetic aspect. The ferromagnetic excitations of local character can be understood well within the spin-wave description. Equations (2.4) and (2.10) show that $a^\dagger_{n:1}$ and $a^\dagger_{n:3}$, creating bosonic excitations on the $Cu^{2+}(2)$ sites, indeed participate in the construction of $\alpha^\dagger_{k:0}$, but any of $a^\dagger_{n:2}$, creating bosonic excitations on the $Cu^{2+}(1)$ sites, does not. Without mediation of bridging spins $\boldsymbol{S}_{n:2}$, any intraplaquette excitation is never movable. Then, what may happen when δ moves away from unity? The spin-wave theory, whether up to $O(S^1)$ or up to $O(S^0)$, predicts that the ferromagnetic and antiferromagnetic excitation modes $\omega_\mp(k)$ are still parallel and the extra ferromagnetic excitation mode between them, $\omega_0(k)$, remains dispersionless. Let us verify the true scenario.

III. BOND-ALTERNATING TRIMERIC CHAINS

We demonstrate in Fig. 3 several schemes of calculating low-lying excitation modes for the spin-$\frac{1}{2}$ bond-alternating trimeric chain. In spite of the persistent flatband within the spin-wave theory, the exact diagonalization reveals that it can be dispersive with varying δ. When $\delta\neq 1$, Hamiltonian (2.1) does not commute with $\boldsymbol{T}^2_{n:3;n+1:1}$. Now that there is a certain probability of composite spins $\boldsymbol{T}_{n:3;n+1:1}$ being singlet even in the ground state, the gapped ferromagnetic excitation mode $\omega_0(k)$ is not describable anymore as their individual triplet-to-singlet flips. At $\delta=0$, any excitation is localized within a trimer of $\boldsymbol{S}_{n:1}$, $\boldsymbol{S}_{n:2}$, and $\boldsymbol{S}_{n:3}$, and the excitation spectrum degenerates into three flatbands, $\omega_-(k)\equiv 0$, $\omega_0(k)=J_1$, and $\omega_+(k)=3J_1/2$. Figure 3 shows that their middle branch connects with the flatband at $\delta=1$. Without J_2, Hamiltonian (2.1) is reduced to

$$\mathcal{H} = \mathcal{H}_1 = J_1\sum_{n=1}^{N}\boldsymbol{S}_{n:2}\cdot\boldsymbol{T}_{n:1;n:3}, \tag{3.1}$$

with intratrimer composite spins $\boldsymbol{T}_{n:1;n:3}\equiv\boldsymbol{S}_{n:1}+\boldsymbol{S}_{n:3}$ and thus commutes with $\boldsymbol{T}^2_{n:1;n:3}$. The plaquette chain [Eq. (2.13)] and the decoupled trimers [Eq. (3.1)] both exhibit a flatband

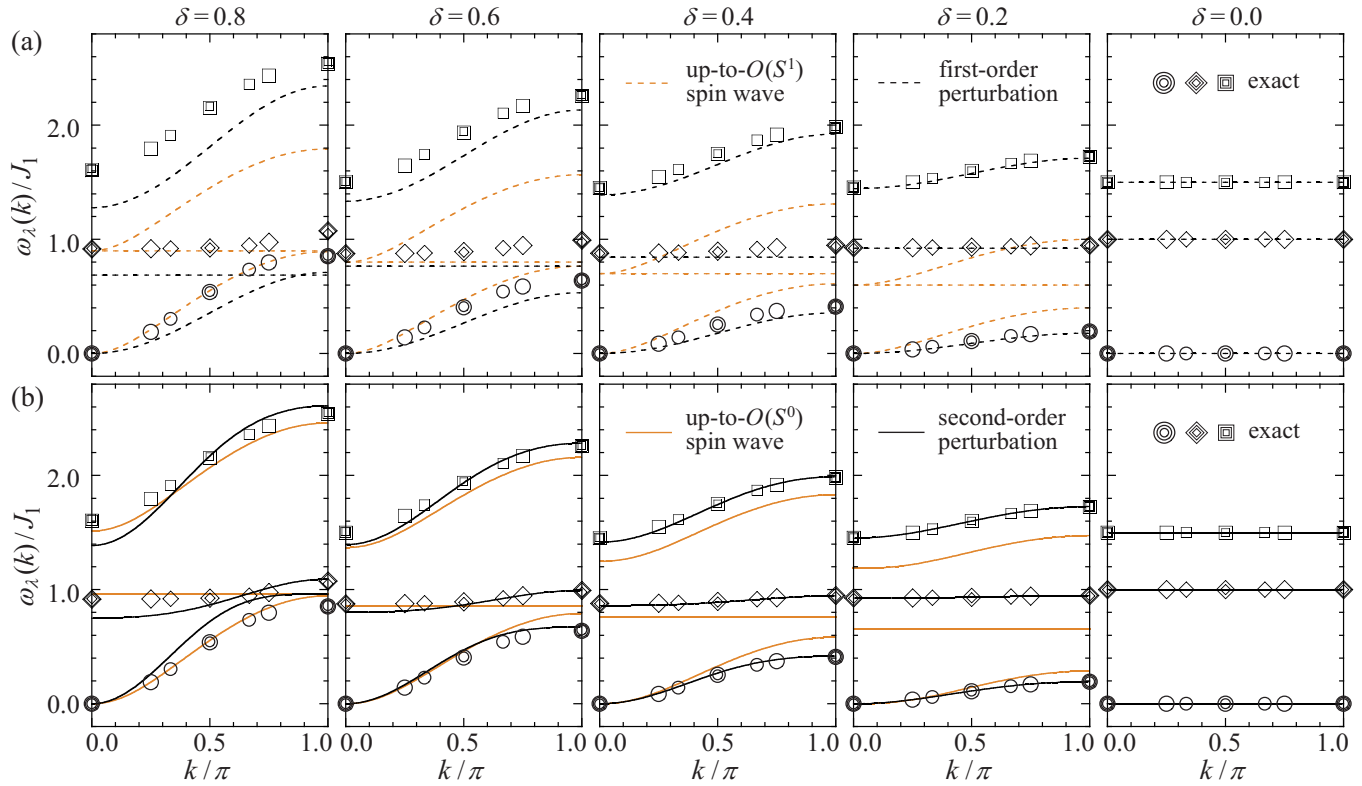

FIG. 3. (Color online) Dispersion relations of the elementary excitations in the spin-$\frac{1}{2}$ trimeric chain with varying δ. The first-order perturbational calculations, together with the up to $O(S^1)$ linear spin-wave findings, are given in the upper five, whereas the second-order perturbational calculations, together with the up to $O(S^0)$ interacting spin-wave findings, are given in the lower five. The exact-diagonalization results at $N=4$, 6, and 8 are presented in both the upper and lower panels by symbols of small, middle, and large sizes, respectively.

due to gapped ferromagnetic excitations, but their ways of constructing local immobile excitations are different from each other. Triplet-to-singlet [$(4S+1)$-fold multiplet breaking in general] flips of intraplaquette composite spins $\boldsymbol{T}_{n:3;n+1:1}$ are the elementary excitations in the former, while those of intratrimer composite spins $\boldsymbol{T}_{n:1;n:3}$ are the elementary excitations in the latter. Figure 4 shows how such composite spins behave in the ground state with varying δ. Neither $\boldsymbol{T}_{n:3;n+1:1}$ nor $\boldsymbol{T}_{n:1;n:3}$ form complete triplets at $0<\delta<1$ due to nonvanishing off-diagonal matrix elements $\langle T_{n:3;n+1:1}=1|\mathcal{H}|T_{n:3;n+1:1}=0\rangle$ and $\langle T_{n:1;n:3}=1|\mathcal{H}|T_{n:1;n:3}=0\rangle$. At the two particular points $\delta=1$ and $\delta=0$, only the $Cu^{2+}(2)$ ion spins $\boldsymbol{S}_{n:1}$ and $\boldsymbol{S}_{n:3}$ constitute the gapped ferromagnetic excitation mode, but otherwise, the $Cu^{2+}(1)$ ion spins $\boldsymbol{S}_{n:2}$ also contribute to that. Without interconnecting spins $\boldsymbol{S}_{n:2}$, any excitation is immobile, whereas with their mediation, all the local excitations can be itinerant and the resultant bands are dispersive.

Perturbational calculations support such a scenario. With increasing couplings J_2 between isolated trimers, the energy dispersion relations grow as follows:

$$\frac{E_g}{J_1 N} = -1 - \frac{\delta}{9} - \frac{869}{2430}\delta^2 + O(\delta^3), \tag{3.2}$$

$$\frac{\omega_-(k)}{J_1} = \frac{4}{9}\delta(1-\cos k) + \frac{\delta^2}{2430}(929 - 474\cos k - 455\cos 2k) + O(\delta^3), \tag{3.3}$$

$$\frac{\omega_0(k)}{J_1} = 1 - 0.389\,70\delta + \delta^2(0.320\,99 - 0.267\,36\cos k + 0.042\,12\cos 2k) + O(\delta^3), \tag{3.4}$$

$$\frac{\omega_+(k)}{J_1} = \frac{3}{2} + \frac{\delta}{18}(7 - 12\cos k) + \frac{\delta^2}{810}(346 - 100\cos k - 109\cos 2k) + O(\delta^3). \tag{3.5}$$

Equations (3.3)–(3.5) are also drawn in Fig. 3. The first-order perturbation points out that not only $\omega_{\mp}(k)$ themselves but also their difference should be dispersive, but it cannot reveal the nonvanishing momentum dependence of $\omega_0(k)$. We cannot reproduce the dispersive middle band until we take account of the second-order perturbation. The lowest ferromag-

netic and antiferromagnetic excitations of decoupled trimers [Eq. (3.1)], gapless and gapped by $3J_1/2$ from the ground state, respectively, are both N-fold degenerate and are expressed as

$$|E_{\mp}(m)\rangle = |-(1\pm 3)J_1/4; 1/2 \mp 1\rangle_m \underset{n\neq m}{\otimes} |-J_1; 1/2\rangle_n$$
$$(m = 1,2,\ldots,N), \tag{3.6}$$

while their gapped ferromagnetic excitations at an energy cost of J_1 are N^2-fold degenerate and are expressed as

$$|E_0(m,m')\rangle = \delta_{mm'}|0;-1/2\rangle_m \underset{n\neq m}{\otimes} |-J_1;1/2\rangle_n + (1-\delta_{mm'})|0;1/2\rangle_m \otimes |-J_1;-1/2\rangle_{m'} \underset{n\neq m,m'}{\otimes} |-J_1;1/2\rangle_n \quad (m,m' = 1,2,\ldots,N) \tag{3.7}$$

in terms of the eigenstates of an isolated trimer $|\boldsymbol{S}_{n:1},\boldsymbol{S}_{n:2},\boldsymbol{S}_{n:3}\rangle$,

$$|-J_1;1/2\rangle_n = (1/\sqrt{6})(|\uparrow\uparrow\downarrow\rangle - 2|\uparrow\downarrow\uparrow\rangle + |\downarrow\uparrow\uparrow\rangle),$$
$$|-J_1;-1/2\rangle_n = (1/\sqrt{6})(|\downarrow\downarrow\uparrow\rangle - 2|\downarrow\uparrow\downarrow\rangle + |\uparrow\downarrow\downarrow\rangle),$$
$$|0;1/2\rangle_n = (1/\sqrt{2})(|\uparrow\uparrow\downarrow\rangle - |\downarrow\uparrow\uparrow\rangle),$$
$$|0;-1/2\rangle_n = (1/\sqrt{2})(|\downarrow\downarrow\uparrow\rangle - |\uparrow\downarrow\downarrow\rangle),$$
$$|J_1/2;3/2\rangle_n = |\uparrow\uparrow\uparrow\rangle,$$
$$|J_1/2;1/2\rangle_n = (1/\sqrt{3})(|\uparrow\uparrow\downarrow\rangle + |\uparrow\downarrow\uparrow\rangle + |\downarrow\uparrow\uparrow\rangle),$$
$$|J_1/2;-1/2\rangle_n = (1/\sqrt{3})(|\uparrow\downarrow\downarrow\rangle + |\downarrow\uparrow\downarrow\rangle + |\downarrow\downarrow\uparrow\rangle),$$
$$|J_1/2;-3/2\rangle_n = |\downarrow\downarrow\downarrow\rangle. \tag{3.8}$$

With perturbational interactions $\mathcal{H}_2$ turned on, the N-fold degeneracy of the eigenvalue $-[N-3(1\mp 1)/4]J_1 = \langle E_{\mp}(m)|\mathcal{H}_1|E_{\mp}(m)\rangle$ is completely lifted, whereas the N^2-fold degenerate eigenvalue $-(N-1)J_1 = \langle E_0(m,m')|\mathcal{H}_1|E_0(m,m')\rangle$ only splits into N flatbands within the first-order corrections. The second-order corrections are necessary for reproducing the dispersion relation of $\omega_0(k)$. In this context, we may be reminded that Honecker and Läuchli[49] pioneeringly investigated analogous but frustrated Cu^{2+} trimeric chains. The gapless ferromagnetic excitation mode [Eq. (3.3)] is indeed derived from their effective Hamiltonian under strong trimerization $\delta \ll 1$.

IV. SUMMARY AND DISCUSSION

We have investigated the low-energy structure of intertwining double-chain ferrimagnets composed of homogeneous spins with particular emphasis on the gapped ferromagnetic excitation mode. While there exist a macroscopic number of flatbands[50] in the excitation spectrum at $\delta=1$ and $\delta=0$, which signify uncorrelated excitations of local spin-$2S$ multiplets in any case, they become dispersive as soon as δ moves away from these particular points. Pair excitations of corner spins $\boldsymbol{S}_{n:3}$ and $\boldsymbol{S}_{n+1:1}$ are elementary in plaquette chains of $\delta=1$, while those of $\boldsymbol{S}_{n:1}$ and $\boldsymbol{S}_{n:3}$ are elementary in decoupled trimers of $\delta=0$, both of which are completely immobile without any mediation of joint spins $\boldsymbol{S}_{n:2}$. The spin-wave theory successfully characterizes the plaquette chain but fails to find arising contribution of $\boldsymbol{S}_{n:2}$ to gapped ferromagnetic excitations with bond alternation. Such a misleading prediction has been corrected by further numerical and analytical investigations.

The spin-S plaquette chain thus shares the whole nature of the alternating-spin-$(2S,S)$ linear chain and further exhibits ferromagnetic excitations of its own. All the findings but the flatband in Fig. 2 are indeed exactly the same as we have in the ferrimagnetic Heisenberg chain of alternating spins 1 and $\frac{1}{2}$.[45] Even though the homogeneous-spin plaquette chain and the alternating-spin linear chain are equivalent in their ground states, the former demonstrates its extra excitation degrees of freedom and deviates from the latter with increasing temperature. In order to illuminate the similarities and differences between them, we show in Fig. 5 quantum Monte Carlo calculations of their static structure factors,

$$S(q) = \frac{1}{N}\sum_{n,l,n',l'} e^{iq(x_{n:l}-x_{n':l'})} S^z_{n:l} S^z_{n':l'}, \tag{4.1}$$

as functions of temperature, where the chain directional coordinates $x_{n:l}$ are given in the unit of neighboring-spin spacing. The pronounced peaks at $q=0$ and $q=\pi$ reflect the ferromagnetic and antiferromagnetic double excitation mechanisms in common. Without any field applied, $S(0)$ and $S(\pi)$ are, respectively, the uniform and the staggered susceptibilities multiplied by temperature. With decreasing temperature, they both diverge as $1/T$.[38,45,51] With increasing temperature, they both approach the paramagnetic value $\Sigma_l S_{n:l}(S_{n:l}+1)/3$ but behave differently at intermediate temperatures. A minimum of $S(0)$ as a function of temperature is

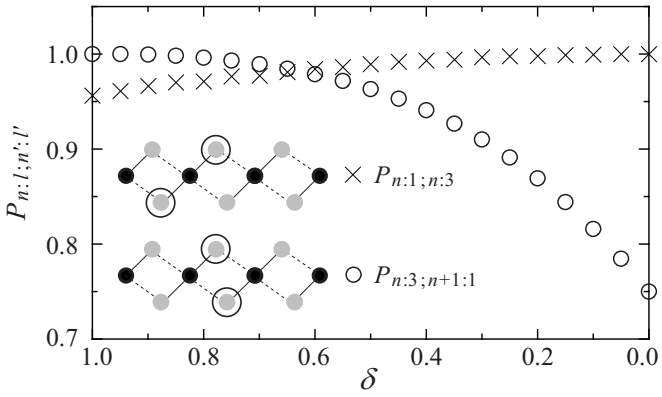

FIG. 4. Probability of two spin $\frac{1}{2}$'s constructing a spin 1 in the ground state of the spin-$\frac{1}{2}$ trimeric chain of $N=64$ with varying δ, where $P_{n:3;n+1:1} \equiv \boldsymbol{T}^2_{n:3;n+1:1}/2 = \boldsymbol{S}_{n:3}\cdot\boldsymbol{S}_{n+1:1}+3/4$ and $P_{n:1;n:3} \equiv \boldsymbol{T}^2_{n:1;n:3}/2 = \boldsymbol{S}_{n:1}\cdot\boldsymbol{S}_{n:3}+3/4$ are estimated by a quantum Monte Carlo method.

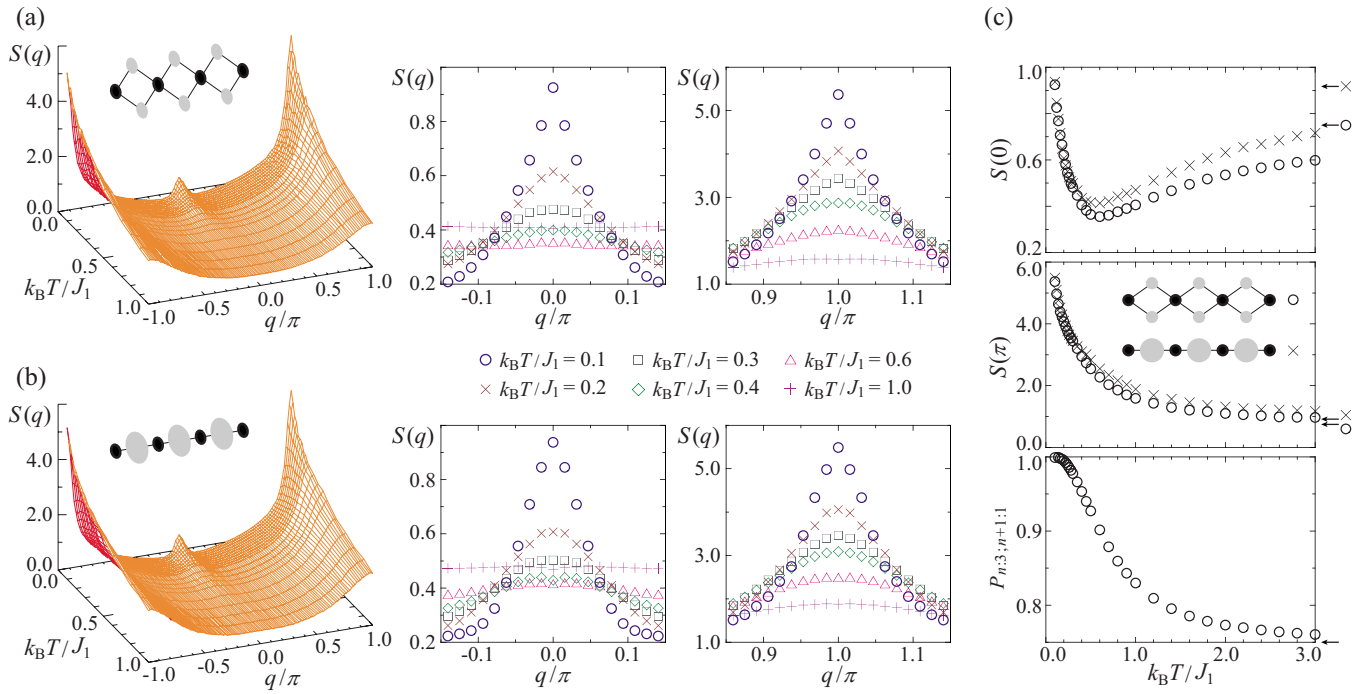

FIG. 5. (Color online) Quantum Monte Carlo calculations of the static structure factor $S(q)$, with the distance between neighboring spins in the chain direction set equal to unity, as a function of temperature. The whole view and enlargements at $q=0$ and $q=\pi$ for (a) the spin-$\frac{1}{2}$ plaquette chain of $N=64$ and (b) the alternating-spin-$(1,\frac{1}{2})$ linear chain of $N=64$. (c) The ferromagnetic $[S(0)]$ and antiferromagnetic $[S(\pi)]$ peaks are observed in more detail, where the common asymptotic values in the high-temperature limit, 3/4 and 11/12 for the spin-$\frac{1}{2}$ plaquette chain and the alternating-spin-$(1,\frac{1}{2})$ linear chain, respectively, are indicated with arrows. Thermal averages of the projection $P_{n:3;n+1:1}\equiv \boldsymbol{T}^2_{n:3;n+1:1}/2=\boldsymbol{S}_{n:3}\cdot\boldsymbol{S}_{n+1:1}+3/4$ in the spin-$\frac{1}{2}$ plaquette chain are also shown for reference, where the asymptotic value in the high-temperature limit, 3/4, is indicated with an arrow.

characteristic of ferrimagnets.[6,7,18,25,30,52–54] $S(0)$ monotonically decreases and increases with increasing temperature in ferromagnets and antiferromagnets, respectively.[14] Though the thermal and quantum behaviors of the spin-S plaquette chain and the alternating-spin-$(2S,S)$ linear chain are very much alike, there grows a difference between them with pair excitations of intraplaquette spins $\boldsymbol{S}_{n:3}$ and $\boldsymbol{S}_{n+1:1}$ from their highest multiplets. The ferromagnetic and antiferromagnetic structures of $S(q)$ survive less with increasing temperature in the spin-S plaquette chain than in the alternating-spin-$(2S,S)$ linear chain. The larger the S, the more major is the difference in $S(q)$ as $\lim_{T\to\infty}[S^{(2S,S)}(q)-S^{(S,S,S)}(q)]=2S^2/3$. Alternating-spin-$(2S,S)$ ferrimagnetic chains behave like combinations of spin-S ferromagnetic and spin-$(2S)$ antiferromagnetic chains,[14] while such a simple magnetic sum rule is not available to intertwining double-chain ferrimagnets of our interest. Additional intraplaquette antiferromagnetic interactions induce incommensurate peaks in $S(q)$,[55] making corner spins $\boldsymbol{S}_{n:3}$ and $\boldsymbol{S}_{n+1:1}$ frustrated.

Once δ moves away from unity, the homogeneous-spin trimeric chain does not share any feature of the alternating-spin chain anymore. Figure 6 presents $S(q)$ with varying δ and analyzes its features at $q=0$ and $q=\pi$, in particular. At low temperatures, $S(0)$ and $S(\pi)$ both decline with decreasing δ, but they still diverge as $1/T$ unless $\delta=0$.[30] At high temperatures, $S(\pi)$ remains decreasing, whereas $S(0)$ increases with decreasing δ. Decoupled trimers are nothing more than paramagnets and their structure factor is given as

$$S(q)=\frac{3}{4}-\frac{2}{3}\frac{e^{J_1/k_BT}-e^{-J_1/2k_BT}}{e^{J_1/k_BT}+1+2e^{-J_1/2k_BT}}\cos q + \frac{1}{6}\frac{e^{J_1/k_BT}-3+2e^{-J_1/2k_BT}}{e^{J_1/k_BT}+1+2e^{-J_1/2k_BT}}\cos 2q, \tag{4.2}$$

which is also drawn in Fig. 6 with solid lines. Equation (4.2)

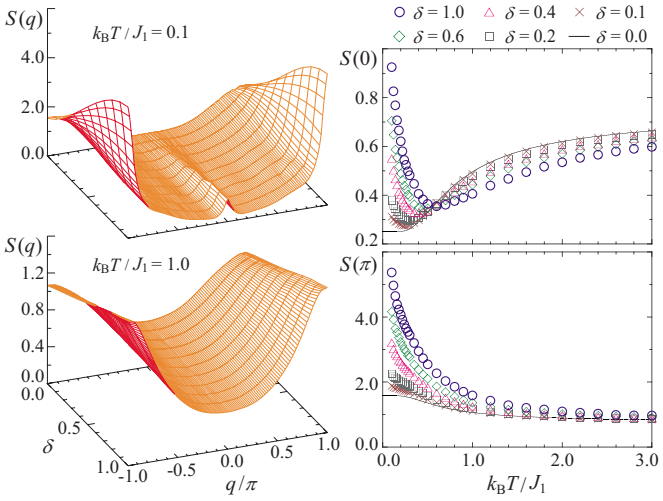

FIG. 6. (Color online) Quantum Monte Carlo calculations of the static structure factor $S(q)$, with the distance between neighboring spins in the chain direction set equal to unity, as a function of bond alternation and temperature for the spin-$\frac{1}{2}$ trimeric chain of $N=64$.

at $q=0$ reads as the effective Curie law for a trimer entity, where the Curie constant varies from 1/4, attributable to the ground-state doublet, to 3/4, simply coming from free spin $\frac{1}{2}$'s, with increasing temperature. Arising intertrimer couplings J_2 immediately pronounce a quadratic dispersion relation of the ferromagnetic excitations at small momenta and their further increase costs the antiferromagnetic excitations higher energy. That is why growing global correlations enhance and reduce the uniform susceptibility-temperature product at low and high temperatures, respectively.

Weak but nonvanishing dispersion of the gapped ferromagnetic excitation mode is our most remarkable finding and is the very characteristic of intertwining double-chain ferrimagnets. As the existent compounds $A_3Cu_3(PO_4)_4$ have all been reported to exhibit rather strong bond alternation $\delta \leq 0.1$,[30,32–35] it may be hard to detect the dispersion relation $\omega_0(k)$ there. Ni analogs, if available, will present an energy structure of the same type on an enlarged energy scale. Highly localized excitations in fully exchange-coupled bulk magnets may either arise from an accidental arrangement of exchange couplings or come out of a particular lattice structure of geometric aspect. While some examples of the former case can be found in spin-$\frac{1}{2}$ bond-polymerized chains in principle,[37,61] it must be hard to observe them in real materials. On the other hand, the present findings are of the latter origin and may be more accessible experimentally. The Shastry-Sutherland lattice[56] is also interesting in this sense and the model compound $SrCu_2(BO_3)_2$ indeed exhibits an excitation mode of little dispersion in its low-energy spectrum.[57] Such local excitations crystallize to form a superlattice, quantizing the ground-state magnetization.[58–60] There may be a similar scenario in low-dimensional ferrimagnets of topological origin as well. We hope the present study will stimulate further experimental explorations.

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