Frustrated spin ladder with alternating spin-1 and spin-1/2 rungs

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We study the impact of the diagonal frustrating couplings on the quantum phase diagram of a two-leg ladder composed of alternating spin-1 and spin-1/2 rungs. As the coupling strength is increased the system successively exhibits two gapped paramagnetic phases (a rung-singlet and a Haldane-like non-degenerate states) and two ferrimagnetic phases with different ferromagnetic moments per rung. The first two states are similar to the phases studied in the frustrated spin-1/2 ladder, whereas the magnetic phases appear as a result of the mixed-spin structure of the model. A detailed characterization of these phases is presented using density-matrix renormalization-group calculations, exact diagonalizations of periodic clusters, and an effective Hamiltonian approach inspired by the analysis of numerical data. The present theoretical study was motivated by the recent synthesis of the quasi-one-dimensional ferrimagnetic material FeIIFeIII (trans-1,4-cyclohexanedicarboxylate) exhibiting a similar ladder structure.

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I. INTRODUCTION

Over the past two decades there has been an increasing interest in quantum spin systems with competing exchange interactions.1-4 Quantum spin chains and ladders with frustration, both for half-integer and integer spins, set up an important part of this research since they provide a unique testing ground based on the available powerful analytical and numerical techniques for one-dimensional (1D) systems. In particular, the frustrated ladder models have allowed controlled calculations to examine topological order,5 dimer order as well as the appearance of fractional excitations in spin models.6,7 Most of previously studied frustrated chain and ladder models have been related to uniform-spin structures with all the spins same. In comparison, till now much less experimental as well as theoretical work concerning the impact of competing interactions in quasi-1D mixed-spin systems has been accomplished.8 Often these systems exhibit quasi-1D ferrimagnetic ground states with a net ferromagnetic moment, so that apart from rich quantum phase diagrams they might be expected to provide generic examples of 1D magnetic-paramagnetic quantum phase transitions.9

On the experimental side, during the past two decades it has become possible to synthesize a large variety of quasi-1D materials with ferrimagnetic properties. Most of these materials are heterometallic molecular magnets containing different transition metal ions in the unit cell.10 A generic spin model describing these materials is the quantum Heisenberg spin chain with antiferromagnetic nearest-neighbor exchange interactions and two types of alternating quantum spins with magnitudes S1 and S2 (S1 > S2).11,12 In the extreme quantum case of spins (1, 1/2), the latter model was shown to provide an excellent description of the thermodynamic parameters of the recently synthesized quasi-1D bimetallic compound NiCu(pba)(D2O)2·2D2O (pba = 1,3-propylenedienic)13. Another important class of quasi-1D ferrimagnets – the so-called topological ferrimagnets – is related to some homometallic materials exhibiting composite chain structures with different magnetic sublattices.14 The homometallic material A3Cu3(P04)4 (A=Ca, Sr, Pb) is an example of such quasi-1D ferrimagnets: In this compound, the Cu2+ ions form diamond chains with strongly coupled trimers bridged by oxygen ions.15 Since quasi-1D homometallic materials usually have rich exchange pathway structures, they may be expected to provide some real examples of quasi-1D ferrimagnets with magnetic frustration. To the best of our knowledge, the recently synthesized mixed-valent magnetic material FeIIFeIII (trans-1,4-cyclohexanedicarboxylate)16 provides the first real example of a quasi-1D Heisenberg ferrimagnet with magnetic frustration.17 The experimentally established magnetic structure for temperatures larger than 36 K corresponds to the mixed-spin ladder with diagonal exchange bonds shown in Fig. 1 where the site spins S1 = 5/2 and S2 = 2 are respectively related to the magnetic ions FeII and FeIII.18

The mentioned experimental achievements motivated a series of theoretical studies on quantum mixed-spin chains and ladders with geometric frustration. The symmetric diamond chain with antiferromagnetic vertical bonds was probably the first studied model of a 1D quantum ferrimagnet with competing interactions.19 A variant of this model, the distorted spin-1/2 diamond chain, has received special theoretical19 as well as experimental20 interest due to its rich quantum phase diagram and the relevance for the real material Cu3(CO3)12(OH)2. The diamond Heisenberg chain
is also one of the simplest quantum spin models admitting four-spin cyclic exchange interactions\textsuperscript{22} A generic quantum spin model of a frustrated 1D ferrimagnet is the mixed-spin Heisenberg chain composed of two types of alternating spins interacting via competing nearest-neighbor and next-nearest-neighbor antiferromagnetic exchange bonds\textsuperscript{22} This model may also be considered as a mixed-spin zigzag ladder and is a ferrimagnetic analogue of the frustrated Heisenberg chain with ferromagnetic nearest-neighbor and antiferromagnetic next-nearest-neighbor exchange bonds. The spin-1/2 frustrated $J_1 - J_2$ ferrimagnetic chain has recently attracted much attention\textsuperscript{25} as it is supposed to describe a number of quasi-1D edge-sharing cuprates, such as Rb$_2$Cu$_2$Mo$_3$O$_7$\textsuperscript{23}, Li$_2$ZrCuO$_4$\textsuperscript{24}, and LiCuVO$_3$\textsuperscript{25}. The latter material exhibits multiferroic properties\textsuperscript{26} as well as an interesting specific phase transition in a magnetic field from an ordered spiral to an ordered modulated-collinear magnetic phases\textsuperscript{27}. There are other two generic types of frustrated mixed-spin ladder models describing two interacting mixed-spin alternating chains. The first one is the checkerboard mixed-spin Heisenberg ladder with frustrating diagonal exchange couplings\textsuperscript{28} and the second one is the two-leg ladder model with two types of alternating rungs presented in Fig.\textsuperscript{1}. Finally, there has been a lot of recent work reporting interesting quantum phase diagrams in different composite Heisenberg chains with ferrimagnetic ground states\textsuperscript{29}

In this study we focus on the effects of frustration on the ground state phase diagram of the mixed-spin ladder shown in Fig.\textsuperscript{1}. In addition to the theoretically interesting question of the effects of frustration in this system, an experimental realization of a closely related system in a mixed-valence iron polymer further motivates us\textsuperscript{15}. In the next section we introduce the model and study some relevant properties of its Hamiltonian. In Section \textsuperscript{III} we give a detailed description of the quantum phases by using an effective Hamiltonian approach inspired by the analysis of data obtained using density-matrix renormalization-group (DMRG) and exact diagonalization (ED) techniques. We conclude in Section \textsuperscript{IV} with a brief summary of the results.

\section{The Model}

The system under consideration (see Fig.\textsuperscript{1}) consists of two equivalent mixed-spin Heisenberg chains (characterized by the nearest-neighbor exchange constant $J_1 > 0$) coupled via rung ($J_1, J_2 > 0$) as well as diagonal ($J_4 \geq 0$) exchange bonds. The Hamiltonian of the system reads as

$$H = H_{12} + H_3 + H_4,$$

where

$$H_{12} = \sum_{n=1}^{L/2} \left( J_1 s_{1,2n} \cdot s_{2,2n} + J_2 \sigma_{1,2n-1} \cdot \sigma_{2,2n-1} \right),$$

$$H_3 = J_3 \sum_{n=1}^{L/2} \sum_{m=1}^{2} \left[ s_{m,2n} \cdot \left( \sigma_{m,2n-1} + \sigma_{m,2n+1} \right) \right],$$

$$H_4 = J_4 \sum_{n=1}^{L/2} \left[ s_{1,2n} \cdot \left( \sigma_{2,2n-1} + \sigma_{2,2n+1} \right) + s_{2,2n} \cdot \left( \sigma_{1,2n-1} + \sigma_{1,2n+1} \right) \right].$$

Here $s_{k,2n}$ and $\sigma_{k,2n-1}$ ($k = 1, 2$) are, respectively, spin-$s_1$ and spin-$s_2$ operators ($s_1 > s_2$), and $L$ is the number of rungs.

It is instructive to present the Hamiltonian in the following form

$$H = H_{12} + \sum_{n=1}^{L/2} \left[ J_n s_{2n} \cdot \left( \sigma_{2n-1} + \sigma_{2n+1} \right) \right] + J_n V,$$

where $J_{s,a} = (J_3 \pm J_4)/2$, and $s_{2n} = s_{1,2n} + s_{2,2n}$ and $\sigma_{2n+1} = \sigma_{1,2n+1} + \sigma_{2,2n+1}$ are rung spin operators. The operator $V$ reads as

$$V = \sum_{n=1}^{L/2} L_{2n} \cdot \left( l_{2n-1} + l_{2n+1} \right),$$

where $L_{2n} = s_{1,2n} - s_{2,2n}$ and $l_{2n} = \sigma_{1,2n} - \sigma_{2,2n}$ are rung vector operators. The following analysis of the zero-temperature quantum phase diagram addresses the extreme quantum case of spins $s_1 = 1$ and $s_2 = 1/2$, and is mainly restricted to the parameter subspace defined by $J_1 = J_2 = J_3 > 0$ and $J_4 \geq 0$. To some extent, such a choice of the parameters is motivated by the experimentally established strengths of the exchange couplings in the ferrimagnetic ladder material Fe$^{II}$Fe$^{III}$ (trans-1,4-cyclohexanedicarboxylate)\textsuperscript{15}

\subsection{Symmetries of the model}

The mixed-spin system inherits some important symmetries of the parent uniform-spin Heisenberg ladder

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{The mixed-spin ladder considered in the paper. The arrows show the classical canted state described by the angles $0 < \phi < \pi/2$ and $0 < \theta < \pi/2$ for the classical spins with magnitudes $S_1$ and $S_2$, respectively. The other two classical phases correspond to spin configurations with $(\phi, \theta) = (0, 0)$ (antiferromagnetic state) and $(\phi, \theta) = (\pi/2, \pi/2)$ (ferromagnetic state).} 
\end{figure}
with diagonal interactions. First, if the parameters $J_3$ and $J_4$ in $\mathcal{H}$ are exchanged, one can recover the original Hamiltonian by exchanging either the spins on the $S_1$ rungs ($s_{1,2n} \leftrightarrow s_{2,2n}$), or the spins on the $S_2$ rungs ($\sigma_{1,2n-1} \leftrightarrow \sigma_{2,2n-1}$). This means that $\mathcal{H}(J_1, J_2, J_3, J_4) = \mathcal{H}(J_1, J_2, J_3, J_4)$. Therefore, the study of the model can be restricted in the region $J_4/J_3 \leq 1$ since the model with $J_4/J_3 > 1$ maps onto the one with $J_4/J_3 < 1$. Because of the same symmetry, the Hamiltonian does not contain mixed products of rung spins and rung vector operators.

The second property of $\mathcal{H}$ concerns the subspace $J_3 = J_4 (J_a = 0)$, when the last term in Eq. (2) disappears. As is the uniform-spin case, in this parameter subspace the Hamiltonian $\mathcal{H}$ commutes with the local operators $s_{2n}^z$ and $\sigma_{2n-1}^z$ ($n = 1, 2, \ldots, L/2$), which means that the rung spins $s_{2n}$ and $\sigma_{2n-1}$ [defined as $s_{2n} = s_{2n}(s_{2n} + 1)$ and $\sigma_{2n-1} = s_{2n-1}(\sigma_{2n-1} + 1)$] are good local quantum numbers. Thus in every sector of the Hilbert space, defined by the sequence $[s_1, s_2, \ldots, s_L]$, the first two terms in Eq. (2) reduce to the constant

$$E_0 = -\frac{L}{2} [J_1 S_1(S_1 + 1) + J_2 S_2(S_2 + 1)]$$

$$+ \frac{1}{2} \sum_{n=1}^{L/2} [J_1 s_{2n}(s_{2n} + 1) + J_2 \sigma_{2n-1}(\sigma_{2n-1} + 1)].$$

Thus Eq. (2) takes the simple form of a Heisenberg spin chain

$$\mathcal{H}_0 = E_0 + \sum_{n=1}^{L/2} J_n s_{2n} \cdot (\sigma_{2n-1} + \sigma_{2n+1}).$$

The above expression for $E_0$ implies that for strong enough rung interactions ($J_1/J_3, J_2/J_3 \gg 1$) the singlet eigenstate of Eq. (4), defined as a product of local rung-singlet states, becomes an exact ground state of the model. This state belongs to the sector $[0, 0, \ldots, 0, 0]$ and can be considered as a prototype of the rung-singlet phase of Eq. (2) discussed below. The following analysis of the quantum phase diagram of Eq. (2) implies that in the extreme quantum limit $S_1, S_2 = (1, 1/2)$ the sectors $[1, 1, \ldots, 1, 1], [1, 2, \ldots, 1, 2]$, and $[1, 1, 1, 2, \ldots, 1, 1, 1, 2]$ also play an important role: In the first sector, the model defined by Eq. (4) is equivalent to the spin-$1$ Haldane chain, whereas in the last two sectors Eq. (4) represents spin-alternating ferrimagnetic chains. The ground states relate to these models appear in the quantum phase diagram of the discussed system.

**B. Classical phase diagram**

The classical phases of Eq. (2) can be described by the angles $\phi$ and $\theta$ (see Fig. 1) which determine the orientations of the classical spins in the $xy$ plane. We consider the parameter subspace defined by $J_1 = J_2 = J_3 = 1$ and $J_4 \geq 0$. The expression for the ground-state energy per cell containing two rungs is seen to be

$$\frac{E_c}{S_1 S_2} = \frac{S_1}{S_2} \cos(2\phi) - \frac{S_2}{S_1} \cos(2\theta)$$

$$-4 \cos(\phi - \theta) + 4J_4 \cos(\phi + \theta).$$

A minimization using the independent angle variables $\phi$ and $\theta$ gives the following equations:

$$\cos(\phi + \theta) = \frac{c_1}{\kappa} J_4 - c_2$$

$$\cos(\phi - \theta) = c_2 J_4 - c_1 \kappa,$$

where $c_1 = \sigma - \sigma^{-1}$, $c_2 = \sigma + \sigma^{-1}$, and $\sigma = S_1/S_2 > 1$. The parameter $\kappa = \kappa(J_4)$ reads $\kappa = (4J_4^2/3 - 1/3)^{1/2}$.

The lower ($J_4^{(d)}$) and the upper ($J_4^{(u)}$) phase boundaries of the classical canted phase shown in Fig. 1 are related to the inequalities $|\cos(\phi + \theta)|, |\cos(\phi - \theta)| \leq 1$ implying

$$J_4^{(d)} = \frac{c_2 + 1}{\sqrt{4(c_2 + 1)^2 - 3c_1^2}},$$

$$J_4^{(u)} = \frac{c_2 - 1}{\sqrt{4(c_2 - 1)^2 - 3c_1^2}}.$$

**FIG. 2:** (a) The classical phase diagram described by the angles $\phi$ and $\theta$ vs. $J_4$, as obtained from Eq. (5) for the system with $S_1 = 1$ and $S_2 = 1/2$. (b) $x$ components of the classical magnetizations in the $S_1 (M_1)$ and $S_2 (M_2)$ sites of the same system. The filled circles on the $J_4$ axis correspond to the classical transition points $J_4^{(d)} = 7/13$ and $J_4^{(a)} = 1$.

For $J_4 < J_4^{(d)}$, we get states of zero magnetization in which the two spins on any rung and spins along a leg are antiferromagnetically aligned. The canted state realized for $J_4^{(d)} < J_4 < J_4^{(u)}$ has a net magnetization that takes a maximal value at some intermediate $J_4$ between both boundaries [see Fig. 2(b)]. For $J_4 > J_4^{(a)}$ this classical canted phase gives way to a ferrimagnetic state where all the spins of the same magnitude are ferromagnetically aligned but the relative alignment of $S_1$ and $S_2$ is antiferromagnetic. Notice that the magnetic measurements in Ref. 17 indicate the discussed ferrimagnetic configuration—eventually with a small canting of the classical spins— as the most probable spin configuration realized in the real material Fe$^I$Fe$^{II}$. For $S_1 = 1$ and $S_2 = 1/2$, the above equations give $J_4^{(d)} = 7/13 \approx 0.538$ and $J_4^{(a)} = 1$. For the real material studied in Ref. 17 ($S_1 = 5/2, S_2 = 2$), one has $J_4^{(d)} = 61/121 \approx 0.504$ and $J_4^{(a)} = 21/39 \approx 0.553$. 
Interestingly, the discussed classical ferrimagnetic state appears only for relatively small values of $\sigma$. For larger $\sigma$, the lowest energy collinear configuration for large $J_4$ is a non-magnetic state with ferromagnetically arranged legs pointing in opposite directions (i.e., antiferromagnetically aligned rungs). Comparing the energies of both configurations ($E_c^{(1)} = S_1^2 + S_2^2 - 4S_1S_2 - 4S_1S_2J_4$, $E_c^{(2)} = -S_1^2 - S_2^2 + 4S_1S_2 - 4S_1S_2J_4$, respectively), we see that the ferrimagnetic configuration is realized only in the interval $1 < \sigma \leq 2 + \sqrt{3} \approx 3.73$. In the large $\sigma$ case, the cantled phase is also modified: On increasing the parameter $J_4$ from $J_4^{(d)}$ up to $J_4^{(o)}$, the $S_2$ spins smoothly change their orientation by $\pi$, whereas the net orientation of the larger $S_1$ spins coincides at the phase boundaries. In both variants of the classical phase diagram the phase boundaries are defined by Eq. (7).

Finally, the discussed classical phase diagrams were independently confirmed by our classical Monte-Carlo simulations. Below we argue that the classical ferrimagnetic phase survives quantum fluctuations, whereas both the antiferromagnetic as well as the cantled classical phases are completely destroyed.

### III. QUANTUM PHASE DIAGRAM

We consider the parameter subspace defined by $J_1 = J_2 = J_3 \equiv 1$ and $0 \leq J_4 \leq 1.5$, and use the DMRG method for open boundary conditions supplemented by ED data for periodic clusters containing up to $L = 14$ rungs. DMRG is carried out for this system for a range of lattice sizes up to $L = 100$ rungs with the spin values $S_1 = 1$ and $S_2 = 1/2$, respectively. Up to 320 density matrix eigenvectors were retained. Depending on the value of $J_4$, the truncation errors are between $10^{-7}$ and $10^{-12}$.

The DMRG results presented in Fig. 3 reveal three special points on the $J_4$ axis separating regions with different characteristics of the short-range correlations: $J_4^{(1)} = 0.710$, $J_4^{(2)} = 0.875$, and $J_4^{(3)} = 0.975$. The same points are also presented in Fig. 3 which shows DMRG results ($L = 90$) for the ground-state energy of the mixed-spin model. A detailed numerical analysis, using both the DMRG and ED methods, predicts singlet ground states: RS (rung-singlet), HL (Haldane-like), and two different ferrimagnetic states ($F_1$ and $F_2$). The straight line $ab$ represents the energy of the Haldane state $\langle \Psi_H | H | \Psi_H \rangle$.

![FIG. 3: Unit-cell isotropic spin-spin correlations as a function of the frustration parameter $J_4$, as obtained from the DMRG method for open boundary conditions ($L = 100$). $J_4^{(1)} = 0.710$, $J_4^{(2)} = 0.875$, and $J_4^{(3)} = 0.975$ are the special points identified as phase-transition points between different ground states. The inset shows the difference in the spin-1 rung correlations in two neighboring cells. Note that the presented spin-spin correlations belong to unit cells far from the ends.](image1)

![FIG. 4: Ground-state energy per rung as a function of the frustration parameter $J_4$ (DMRG, $L = 90$). $J_4^{(1)} = 0.723$ denotes the location of the maximum. The positions of the special points identified in Fig. 3 separate different ground states: RS (rung-singlet), HL (Haldane-like), and two different ferrimagnetic states ($F_1$ and $F_2$). The straight line $ab$ represents the energy of the Haldane state $\langle \Psi_H | H | \Psi_H \rangle$.](image2)

A. Mapping onto the frustrated spin-1/2 ladder

An inspection of the short-range correlations presented in Fig. 3 implies that the weight of the local rung quintet (i.e., $s_{2n} = 2$) states on the spin-1 rungs is negligible almost in the whole interval $0 \leq J_4 < J_4^{(2)}$. Indeed, by using the identity $\langle s_{1,2n} \cdot s_{2,2n} \rangle = (\langle s_{2n}^2 \rangle - 3/2)/2 - 5/4$, one finds that the following relation between the average rung correlations should be satisfied for any state with a zero weight of the rung quintet states:

$$\langle s_{1,2n} \cdot s_{2,2n} \rangle = \langle \sigma_{1,2n-1} \cdot \sigma_{2,2n-1} \rangle - \frac{5}{4}. \quad (8)$$
As seen from the numerical results, the above relation is almost perfectly fulfilled in the entire region $0 \leq J_1 < J_4^2$, excluding some narrow vicinity of the point $J_4^2$ where the correlations $\langle s_{1,2n} \cdot s_{3,2n} \rangle$ abruptly change to $\approx 1$. The extremely small contribution of the quantum rung states in the region $0 \leq J_4 < J_4^2$ can be explained by the peculiarities of the energy spectrum of the mixed-spin plaquette, where the lowest quantum state happens to be well separated from the low-lying triplet and singlet states. Note that the excitation of local triplet states is controlled by the last term $(V)$ in the Hamiltonian (2). Thus, starting from an eigenstate belonging to the sector $s_{2n}, \sigma_{2n-1} = 0, 1 \ (n = 1, \ldots, L/2)$, the first-order corrections to the wave function of this eigenstate will contain relatively small amount of configurations belonging to the sectors with local quantum states due to the larger energy denominator in the perturbation expression.

These observations suggest, in particular, that in the discussed region the ground-state properties of the mixed-spin system may be approximately interpreted by projecting out the local quantum states in the mixed-spin Hamiltonian (2). Up to first order in $J_4$, the projected Hamiltonian reads as (see the Appendix)

$$\mathcal{H}_{\text{eff}} = -\frac{5}{8} JL + \sum_{n=1}^{L} \left[ J'_1 \sigma_{1,n} \cdot \sigma_{2,n} + J'_n \sigma_{n} \cdot \sigma_{n+1} + J'_l n \cdot l_{n+1} \right],$$

(9)

where $\sigma_{1,n}$ and $\sigma_{2,n}$ are spin-1/2 operators, $\sigma_{n} = \sigma_{1,n} + \sigma_{2,n}$, $l_{n} = \sigma_{1,n} - \sigma_{2,n}$, $J'_1 = J'_2 = J_1$, $J'_s = J_s$, and $J'_a = -2\sqrt{2/3} J_a$. For simplicity, we have restricted ourselves to the case of equal rung couplings ($J_1 = J_2 = J_3$). The effective Hamiltonian (9) describes a frustrated spin-1/2 Heisenberg ladder characterized by three parameters, i.e., the strength of the rung ($J'_1$), leg ($J'_3 = J'_s + J'_a$), and diagonal ($J'_4 = J'_a - J'_s$) exchange bonds. Using the same reasoning, it may be safely suggested that the next-order corrections in $J_4$ do not change substantially the singlet ground states, so that the effective Hamiltonian (9) may be used (i) to identify the singlet ground states of the original Hamiltonian (2) in the region $0 \leq J_4 < J_4^2$ and (ii) to analyze the related quantum phase transitions.

As is well-known, as a function of the frustration parameter $J'_4$ the model (9) exhibits the so-called rung-singlet (RS) and Haldane-like (HL) phases. Both ground states are non-degenerate and exhibit finite singlet-triplet gaps. The character of the quantum RS-HL transition in the weak-coupling limit is still under debate: Some of the cited works suggest a direct first-order transition between these phases, while others predict an intermediate columnar dimer phase. Thus the mapping of Eq. (9) implies that the special point $J_4 = J_4^1$ can presumably be identified as a quantum phase transition point separating similar phases. Of course, such an analysis does not exclude the presence of some intermediate singlet phases in a tiny interval between the RS and HL states. Some hints in this direction inspired by the DMRG results for the ground-state energy (Fig. 1) will be discussed below in more detail.

The established connection with the frustrated spin-1/2 ladder model is additionally supported by the fact that the special point $J_4^1$ perfectly maps on the RS-HL phase boundary in the phase diagram of the frustrated spin-1/2 ladder model\textsuperscript{29}. Indeed, taking the parameters $y_1 = J'_1/J_3$ and $y_2 = J'_4/J_3$ used in Ref. 30, the established relations $J'_4 = J'_s$ and $J'_a = -2\sqrt{2/3} J_a$ between the parameters of the original and the projected Hamiltonians take the form

$$y_1 = \frac{J_1/J_3}{b_2 J_4/J_3 - b_1}, \quad y_2 = \frac{b_2 - b_1 J_4/J_3}{b_2 J_4/J_3 - b_1}, \quad (10)$$

where $b_1 = \sqrt{2}/3 - 1/2$ and $b_2 = \sqrt{2}/3 + 1/2$. Note that the change of $J_4$ (at fixed $J_1 = J_3 = 1$) corresponds to a run in the $(y_1, y_2)$ plane on the ab line (see Fig. 5) defined by $y_2 = (b_1/b_2 + 1)y_1 - b_1/b_2$. Following Ref. 30, we may identify the position of the quantum phase transition with the point $J_4 = J_4^1 \approx 0.710$, at which the spin-1/2 rung correlations change their sign (see Fig. 6). We find that the $(y_1, y_2)$ image $\mathcal{A}$ of the transition point $J_4^1$ maps perfectly on the phase boundary in the $(y_1, y_2)$ plane. In Figure 5 we also show the symmetric point $\bar{A}$ obtained by the coordinate transformations $y_1 \rightarrow y_1/y_2$ and $y_2 \rightarrow 1/y_2$, which are related to the exchange symmetry $J_3 \leftrightarrow J_4$ of the Hamiltonian. As expected, the symmetric point $\bar{A}$ also lies on the phase boundary.
The discussed mapping of Eq. (2) on the frustrated spin-1/2 ladder model suggests that the HL phase should occupy some region in the phase diagram for $J_4 > J_3^1$. To reveal the peculiarities of the suggested HL phase – as compared to the well-known Haldane phase of the periodic spin-1 Heisenberg chain – notice that in the sector $[1, 1, \ldots, 1]$ the Haldane state $|\Psi_H\rangle$ is the exact ground state of the mixed-spin Hamiltonian (2) at the symmetric point $J_3 = J_4$. In the general case ($J_3 \neq J_4$), the energy of this state $E_H = \langle \Psi_H | H | \Psi_H \rangle$ reads as

$$\frac{E_H}{L} = \frac{J_1}{2} + \frac{J_2}{8} + \frac{1}{2} (J_3 + J_4) \varepsilon_H,$$  \hspace{1cm} (11)$$

where $\varepsilon_H = -1.40148403897(4)$ is the the ground-state energy per bond of the periodic spin-1 Heisenberg chain. Here, we have used the fact that the operator $V$ [Eq. (3)] does not have non-zero matrix elements in the sector $[1, 1, \ldots, 1]$: In particular, we have $\langle \Psi_H | V | \Psi_H \rangle = 0$. The energy of the Haldane state $E_H$ as a function of $J_4$ ($J_1 = J_2 = J_3 = 1$) is shown in Fig. (the $ab$ line). Interestingly, at the special point $J_4 = J_4^2 \equiv 0.875$ – also related to an abrupt change of the spin-1 rung correlations – the DMRG estimate for the ground-state energy of the Hamiltonian $E/L = -1.6899$ almost coincides with the energy of the Haldane state $(E_H/L = -1.6889)$ obtained from Eq. (11). As already mentioned above, the numerical analysis implies that the special point $J_4^2$ is a quantum phase-transition point from a singlet non-degenerate state to a state exhibiting a net magnetic moment. The above remarks suggest that the HL phase appears as a good candidate for the phase diagram of the mixed-spin model.

Further qualitative information about the characteristics of this phase can be extracted from a perturbative analysis starting from the symmetric point $J_3 = J_4$ and based on the Haldane state in a periodic spin-1 chain. Note that in some interval $(J_3 < J_4^2)$ the parameter $J_a$, which controls the $V$ term in Eq. (2), may be used as a small parameter (e.g., $J_a = 0.0625$ for $J_3 = 0.875$). Thus, up to second order in $J_a$, the ground-state energy takes the form $E = E_H - const \times (1 - J_4^2)^2 L$, where $const$ is some positive number of order one. Qualitatively, this result reproduces the behavior of the ground-state energy in the interval $J_4^1 < J_3 < J_4^2$ extracted from the DMRG analysis (see Fig. 4). To some extent, this result also validates the choice of $|\Psi_H\rangle$ as a starting unperturbed state.

As compared to the Haldane state, some peculiarities of the HL phase can be revealed by looking at the first-order correction in $J_a$, to the wave function $|\Psi_H\rangle$,

$$|\Psi\rangle = |\Psi_H\rangle + J_a \sum_{n \neq \delta} \frac{|\Psi_n\rangle V |\Psi_H\rangle}{E_0 - E_n} + O(J_a^2).$$  \hspace{1cm} (12)$$

Here the sum runs over the excited eigenstates $|\Psi_n\rangle$ of the Hamiltonian (2) at $J_3 = J_4$, and $E_0 \equiv E_H$. The matrix elements of $V$ (see the Appendix) admit only two
types of excited states ($|\Psi_{1,2}\rangle$) defined, respectively, in the sectors $[1,\ldots,1,0,0,1,\ldots,1]$ (two neighboring rungs in singlet states) and $[1,1,\ldots,1,2,0,1,\ldots,1]$ (one rung in a a quintet state and a neighboring rung in a singlet state). The weights of both types of defect configurations in the HL state change in the interval $J_4^1 < J_4 < J_4^2$: While the weight of the $|\Psi_1\rangle$ configurations grows in a region around the transition point $J_4^1$, the $|\Psi_2\rangle$ configurations (containing spin-2 defects) become visible in the DMRG result for the spin-1 rung correlations only in a short interval preceding the transition to a magnetic state (see Fig. 3). Note that the observed increase of the weight of the $|\Psi_2\rangle$ configurations formally contradicts the perturbation result in Eq. (12), which predicts the opposite behavior. A reasonable resolution for this is provided by the guess that close to the transition point $J_4^2$ some of the eigenenergies $E_n$ related to the sector $[1,1,\ldots,1,2,0,1,\ldots,1]$ soften. As of now we do not have firm numerical results in favor of such a suggestion, although some preliminary DMRG results, using open boundary conditions, seem to predict strong reductions of the singlet-quintet and triplet-quintet gaps close to $J_4^2$.

3. The RS-HL transition

Turning to the region around the transition point $J_4^1$, it is instructive to comment on our numerical results for the excitation gaps (Fig. 7) in the light of the discussed mapping to the spin-1/2 ladder model. For the latter model, it has been numerically established that (i) the lowest state above the singlet ground states close to the phase boundary is a singlet excitation and (ii) the low-lying triplet excitations are gapped in the whole region of the phase diagram in Fig. 3 including the phase-transition boundary. Such a structure of the low-lying excitations is consistent with the established first-order phase-transition boundary. As already mentioned, the character of the RS-HL transition in the weak-coupling limit ($J_1^1, J_4^1 \ll J_3^1$) is still under debate. As a matter of fact, there are some indications for a second-order RS-HL transition and an intermediate dimer phase, but the debate concerns only the weak-coupling part of the phase boundary. Looking at the coordinates of the $A$ and $A'$ images of the transition point $J_4^1$ (Fig. 3), it is clearly seen that the discussed RS-HL transition at $J_4 = J_4^1$ does not belong to the weak-coupling region. Hence, one may expect a first-order RS-HL transition at $J_4^1$ related to a level crossing of singlet ground states.

Figure 7 presents our numerical (DMRG and ED) results for the singlet ($\Delta_s$) and triplet ($\Delta_t$) gaps of the lowest excited modes above both singlet ground states. Let us first discuss the ED data for the gaps. As clearly seen, both minima, related to the $\Delta_s$ and $\Delta_t$ data points, are located close to the expected transition point at $J_4 = 0.710$. More importantly, an extrapolation of the ED data for $J_4 = 0.710$ implies that the $\Delta_s$ points scale to smaller values than $\Delta_t$. This observation is consistent with the expected low-energy structure close the first-order transition point between the RS and HL phases.

Turning to the DMRG results for $\Delta_t(J_4)$, one observes that the triplet gap of the RS phase takes very small values close to the suggested transition point ($J_4 = 0.710$). We could not conclusively exclude the possibility of a gapless triplet excitation at the transition point. In any case, such a behavior indicates some peculiarities of the RS-HL transition in the mixed-spin system, as compared to the uniform-spin case. Another issue to be noticed is the steep (but definitely finite) slope of the function $\Delta_t(J_4)$ at the transition point. This suggests a relatively large correlation length of this triplet excitation close to $J_4^1$.

C. Ferrimagnetic phases

Looking at the DMRG results for the short-range correlations (Fig. 3), it is easy to realize that a ferrimagnetic phase, closely related to the ferrimagnetic ground state of an antiferromagnetic Heisenberg chain with alternating (2, 1) spins, is stabilized around the symmetric point $J_4 = 1$. Exactly at $J_4 = 1$, the ground state of the Hamiltonian belongs to the sector $[1,2,\ldots,1,2]$, so that both models are equivalent in the low-energy sector of the spectrum. The discussed ferrimagnetic phase ($F_1$) exhibits the magnetic moment per rung $M_0 = 1/2$ and
survives almost in the entire region after $J_4^{c2}$, excluding some narrow interval in the vicinity of the latter point. This is also seen in Fig. 8(a) which shows a typical behavior of the local magnetizations $\langle s_{1,2n}^z \rangle$ and $\langle \sigma_{1,2n+1}^z \rangle$ ($n = 1, \ldots, 50$) along the first leg as a function of the site index. The data shown is for $J_4 = 1.55$. (b) The spin-1 rung correlations along the length of the ladder ($L = 100$) at $J_4 = 0.90$. The values show a clear alternation between $\approx 1$ and $\approx -1$ which indicates a two sublattice structure and a doubled unit cell containing four rungs.

FIG. 8: (a) The local magnetizations $\langle s_{1,2n}^z \rangle$ and $\langle \sigma_{1,2n+1}^z \rangle$ ($n = 1, \ldots, 50$) along the first leg as a function of the site index. The data shown is for $J_4 = 1.55$. (b) The spin-1 rung correlations along the length of the ladder ($L = 100$) at $J_4 = 0.90$. The values show a clear alternation between $\approx 1$ and $\approx -1$ which indicates a two sublattice structure and a doubled unit cell containing four rungs.

In conclusion, we have analyzed the combined effect of the quantum fluctuations and the competing interactions in a mixed-spin ladder composed of spin-1 and spin-1/2 rungs which is closely related to a recently synthesized quasi-1D ferrimagnetic material. A comparison of the classical and quantum phase diagrams reveals the following changes in the related quantum system. As expected, the classical ferrimagnetic phase also presents in the quantum phase diagram, but there appears another two-fold degenerate ferrimagnetic state which breaks the translational symmetry. As may be expected, the classical Néel state does not survive quantum fluctuations. More interestingly, the classical canted state also completely disappears. This is in contrast to some other 1D spin systems exhibiting classical canted states where this type of classical magnetic order partially survives quantum fluctuations. In the present case, both the classical long-range ordered states are replaced by two singlet non-degenerate gapped states (RS and HL).

Turning to the weakly frustrated region, it has been established that the behavior of the system strongly resembles that of a two-leg spin-1/2 Heisenberg ladder with frustrating diagonal interactions. However, concerning the quantum phase transition between the RS and HL phases, we have found a few indications demonstrating some peculiarities (such as the extremely small triplet gap at the transition point) of the mixed-spin system. These issues deserve further investigations.

Finally, although the available experimental results on the ferrimagnetic ladder material Fe$^{11}$Fe$^{11}$ (trans-1,4-cyclohexanedicarboxylate) seem to point toward the realization of the $F_1$ ferrimagnetic state, a detailed comparison with the experiment requires a more extensive analysis of the quantum phase diagram including, e.g., different rung couplings $J_1 \neq J_2$, different pairs of rung spin magnitudes, and some anisotropies. Concerning the condition $J_3 = 1$, as shown in Fig. 8(b) it simply restricts the path in the more general parameter space ($J_3 \neq 1$) to a straight line crossing one and the same phase boundary. Therefore, there should be a relatively large region with $J_3 \neq 1$ showing the same structure of the phase diagram. As to the second restriction ($J_1 = J_2$), its removal may be generally expected to bring new quantum spin phases. However, in both cases we have numerically checked that relatively small deviations from the conditions $J_1 = J_2 = J_3$ do not bring qualitative changes on the established quantum phase diagram.

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Appendix: Projection onto the spin-1/2 ladder

We have to project the spin-1 rung states onto the states of the spin-1/2 rungs. To this end, we use the projection operator $P = P_1 P_2 \ldots P_L$, where the rung projection operator $P_n$ reads as

$$P_n = \sum_{\alpha} |T_{2n}^\alpha\rangle\langle T_{2n}^\alpha|, \quad \alpha = 0, x, y, z. \quad (A.1)$$

Here $|T_{2n}^n\rangle$ denotes the singlet state of the 2nth spin-1 rung and $|T_{2n}^x\rangle = (i/\sqrt{2})e^{i\phi} |l\rangle |m\rangle$ are the triplet states of the same rung in a vector basis which is a tensor product of the vector bases of the spin-1 objects (i.e., $|x\rangle$, $|y\rangle$, and $|z\rangle$). In the following, the Greek indices take the values 0, $x$, $y$, and $z$, whereas the Latin ones – $x$, $y$, and $z$.

Up to first order in $J_n$, the projected Hamiltonian reads as

$$H_{eff} = PHP. \quad (A.2)$$

By using the expressions for the matrix elements $\langle T_{2n}^m | s_{2n}^\alpha | T_{2n}^n \rangle = 2\delta^m_0$, $\langle T_{2n}^m | L_{2n}^k | T_{2n}^n \rangle = \langle T_{2n}^m | L_{2n}^l | T_{2n}^n \rangle = 0$, and $\langle T_{2n}^m | T_{2n}^l | T_{2n}^n \rangle = -2\sqrt{2}/3 \delta^{m^2}$, one obtains

$$P_n s_{2n}^2 P_n = 2 \sum_k |T_{2n}^k\rangle\langle T_{2n}^k| = \sigma_{2n}^z, \quad (A.3)$$

where $\sigma_{2n}$ is an effective rung-1/2 spin operator, and

$$P_n V_n P_n = -2 \sqrt{3/3} \sum_k \left[ |T_{2n}^0\rangle\langle T_{2n}^k| + |T_{2n}^k\rangle\langle T_{2n}^0| \right] (I_{2n-1}^k + I_{2n+1}^k).$$

Note that the operator in the square brackets is an effective $l_{2n}$ rung vector operator for spin-1/2 rungs. Summing the above results, we obtain the effective spin-1/2 ladder model presented in Eq. (4).

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