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On the effect of a regular $S = 1$ dilution of $S = 1/2$ antiferromagnetic Heisenberg chains obtained from quantum Monte Carlo simulations

Fengping Jin, Zhaoxin Xu[1], Heping Ying and Bo Zheng

Zhejiang Institute of Modern Physics, Zhejiang University, Hangzhou 310027, People's Republic of China

E-mail: zxxu@zimp.zju.edu.cn

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Abstract

The effect of an $S^1 = 1$ regular dilution in an $S^2 = 1/2$ isotropic antiferromagnetic chain is investigated with quantum Monte Carlo simulations. Our numerical results show that there exist two kinds of ground state phases with different variations of the $S^1 = 1$ concentration. When the effective spin in a unit cell is half-integer, the ground state is ferromagnetic with a gapless energy spectrum, and the magnetism is continuously weakened as the spin S^1 concentration ρ decreases. When the effective spin in a unit cell is integer, however, a non-magnetic ground state with a gapped energy spectrum emerges, and the gap decays gradually, with $\Delta \approx 1.25\sqrt{\rho}$.

1. Introduction

The substitution of magnetic impurities in the antiferromagnetic (AF) spin chain has attracted great interest in the past decade. It is theoretically observed that the ground state properties vary with different dilutions. When the substitution is random, the most interesting case is the Haldane chain [1] with $S = 1/2$ impurities. For example, experiments involving inelastic neutron scattering on the compound Y_2BaNiO_5 substituting Ca^{2+} for Ni^{2+} [2] show a substantial increase of the spectral function below the Haldane gap, indicating the creation of states below the energy of the spin gap. This effect has been studied numerically by Wessel and Haas [3].

For regular substitutions, the system can be described as a mixed-spin chain, this topic has been focused on in the past few years [4, 5]. Analytical approaches to this subject include those of the non-linear sigma model, the mean field theory, and the spin-wave method [6–9]. Numerically, density matrix renormalization group [10] and quantum Monte Carlo (MC) methods [11, 12] have also been extensively applied. It is already well known that the topology

[1] Author to whom any correspondence should be addressed.

of spin arrangements in the mixed-spin chains plays an essential role in the ground state properties and thermodynamics of the mixed-spin systems.

Many quasi-one-dimensional mixed-spin materials have been synthesized in the past two decades, such as $ACu(pba)(H_2O)_3{\cdot}n(H_2O)$ and $ACu(pbaOH)(H_2O)_3{\cdot}nH_2O$ (where pba = 1,3-propylenebis(oxamato), pbaOH = 2-hydroxo-1,3-propylenebis, and A = Ni, Fe, Co, Mn, Zn). These materials contain two kinds of transition metal ions in a unit cell; their properties can be characterized with ferromagnetic chains [13–16], and the magnetic properties of such mixed-spin compounds can be described by a Heisenberg model with the nearest-neighbour antiferromagnetic (AF) couplings:

$$H = \sum_{i=1}^{N} J_i S_i \cdot S_{i+1}, \tag{1}$$

where S_i denotes a spin-S magnet at site i, N is the system size, and the coupling constant $J_i > 0$. Fukui and Kawakami [6] have studied an extension of this system, i.e., a periodic array of S^1 impurities embedded in the host $S^2 \neq S^1$ chain with a period K:

$$\underbrace{S^1 \otimes S^2 \otimes S^2 \otimes \cdots \otimes S^2}_{K} \otimes S^1 \otimes S^2 \otimes \cdots \otimes S^2. \tag{2}$$

There are two dilution limits of the model, denoted by the impurity concentration $\rho = 1/K$: (i) $\rho = 0$, the undoped pure AF chain with a non-magnetic ground state; (ii) $\rho = 0.5$, the alternating array of S^1–S^2 chains. According to the Marshall theorem and the Lieb–Schultz–Mattis (LSM) theorem [17], the ground state of generally doped systems can be specified by a spin quantum number $S = 0(|S^1 - S^2|N/K)$ for the K = odd (even) case and it is a spin singlet (ferrimagnetic). If the effective spin S_{eff} in a K-spin cell is half-integer, the system has a gapless energy spectrum. If S_{eff} is integer, the LSM theorem fails to predict whether the energy spectrum is gapped or gapless. In a theoretical study based on the non-linear σ model, an energy gap is reported [6, 7]. However, details of ground state properties and thermodynamics are not provided in such an analysis.

Recently, the authors of the present paper have been engaged with the model for $S^1 = 1/2$ and $S^2 = 1$ with the quantum loop/cluster algorithm [18, 21]. Numerical results reveal non-trivial magnetic properties for two kinds of regular dilutions. For even K, i.e., an odd number of $S^2 = 1$ spins in a unit cell, the system has a magnetic ground state and shows ferromagnetic features, while for odd K, the system enters a non-magnetic ground state with AF-like character. For both cases, the ground states are all gapless. The doped system gradually turns from the ferrimagnetic ground state of the alternating S^1–S^2 chain to the disordered ground state of a pure spin-1 AF chain, following two tendencies with decreasing impurity concentrations.

In this paper, we will study the opposite case, $S^1 = 1$ and $S^2 = 1/2$. Previous analytical work predicted that if there an odd number of $S^2 = 1/2$ spins in a cell, i.e., S_{eff} is half-integer, the ground state is ferrimagnetic with a gapless energy spectrum, while if there are an even number of $S^2 = 1/2$ spins in the cell, i.e., S_{eff} is integer, the ground state is non-magnetic and the system keeps its energy gap. Our study will focus on how the ground state properties depend on the $S^1 = 1$ concentration ρ and how the magnetic properties at finite temperatures change as ρ decreases.

2. Calculation and results

We perform the MC simulation with the efficient continuous imaginary time version of the loop cluster algorithm [20]. The algorithm has been successfully applied to other mixed-spin chains [18, 21]. The reliability and accuracy of the algorithm have been numerically verified in

calculations of the ground state energy, the energy gap, and the uniform magnetic susceptibility for different models, including the pure spin $S = 1$ chain, and the alternating $1\text{–}\frac{1}{2}$ and $1\text{–}\frac{3}{2}$ mixed-spin chains. Within acceptable numerical errors [22], the results obtained are consistent with the analytical calculations [12] and other numerical results obtained with density matrix renormalization group methods and quantum MC simulations [10, 12, 19, 23]. Thus we believe that the current MC simulation is also efficient and credible for the model investigated in this paper.

We confine our study to the case of homogeneous AF couplings ($J_i = J > 0$), and the positions of the spin $S^1 = 1/2$ and $S^2 = 1$ are arranged according to equation (2) for K ranging from 2 to 11. After 10^3 MC time steps for thermalization, 10^5 MC time steps are carried out for calculating physical quantities. In order to clarify the ground state properties, the simulations are performed at a very low temperature, $\beta = 1/T = 200$, for system sizes of $L \sim 200$ under the condition of an even number of unit cells in the chain. The measured physical quantities are the ground state energy E_{G}, the uniform magnetic susceptibility χ_{u}, and the staggered susceptibility χ_{s}, using improved estimators in the loop cluster algorithm:

$$\langle \chi \rangle = \frac{\beta}{4V} \left\langle \sum_{\text{cluster } c} w_t(c)^2 \right\rangle_{\mathrm{MC}}, \tag{3}$$

$$\langle \chi_{\mathrm{s}} \rangle = \frac{1}{4V\beta} \left\langle \sum_{\text{cluster } c} |C|^2 \right\rangle_{\mathrm{MC}}, \tag{4}$$

where $w(c)$ is the winding number of a cluster c and $|C|$ is the cluster size. The magnetization and staggered magnetization are defined by

$$\langle M^2 \rangle = \left\langle 3 \left(\sum_i S_i^z \right)^2 \right\rangle_{\mathrm{MC}} \tag{5}$$

and

$$\langle M_{\mathrm{s}}^2 \rangle = \left\langle 3 \left(\sum_i (-1)^i S_i^z \right)^2 \right\rangle_{\mathrm{MC}}, \tag{6}$$

respectively, and the energy gap Δ is estimated in the same way as given by Todo and Kato [23]:

$$\Delta = \lim_{L \to \infty} \frac{1}{\xi_{\tau,0}(L)}, \tag{7}$$

where $\xi_{\tau,0}$ is the correlation length in the imaginary time direction.

The results for the magnetization and uniform susceptibility are plotted in figures 1 and 2. The size of the error bars is less than that of the symbols in all figures in this paper. Obviously, the magnetic properties for $K =$ odd and $K =$ even cases are different. For $K =$ even, the magnetization is finite and approaches zero linearly as ρ decreases. For $K =$ odd, the magnetization remains zero. On the other hand, the uniform susceptibility χ_{u} retains finite values for $K =$ even, but vanishes for $K =$ odd. Thus the ground state is ferrimagnetic for $K =$ even, but non-magnetic for $K =$ odd.

Next, we measured the staggered magnetization and staggered susceptibility; their dependences on the concentration ρ are shown in figures 3 and 4 respectively. Both quantities are finite for the $K =$ odd and $K =$ even cases. However, the values for $K =$ even are much bigger than those for $K =$ odd.

In order to confirm the above results, we further investigate the uniform magnetic susceptibility at finite temperatures. As displayed in figure 5, for $K =$ even one can easily see that χ_{u} diverges when the temperature $T = 1/\beta$ goes to zero, and this is a typical behaviour

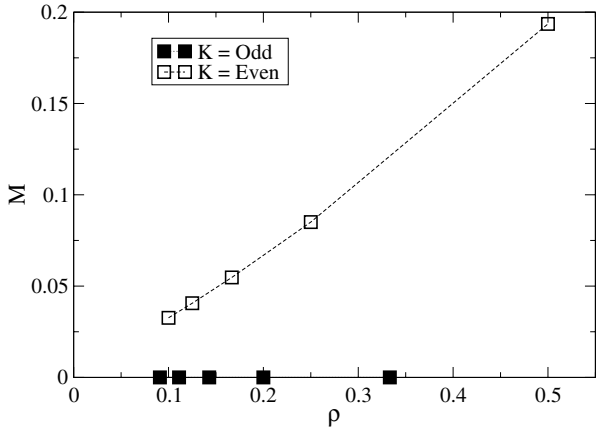

Figure 1. The magnetization versus the dilution concentration $\rho = 1/K$ for $\beta = 200$ and $L \sim 200$. The filled squares present data for $K =$ even and the empty squares, data for $K =$ odd.

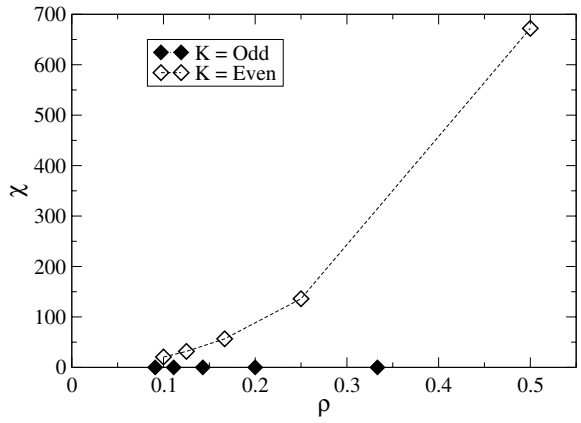

Figure 2. The magnetic susceptibility versus $\rho = 1/K$ for $\beta = 200$ and $L \sim 200$. The filled diamonds present data for $K =$ even and the empty diamonds, data for $K =$ odd.

of a magnetic system. In the $K =$ odd case, χ_u approaches zero when $T \to 0$. We fit the result for χ_u versus T for the $K = 3$ case (the $1{-}\frac{1}{2}{-}\frac{1}{2}$ mixed-spin chain) with the activated behaviour $\chi_u \sim e^{-\Delta/T}$ and obtain $\Delta \sim 0.57$. This result is consistent with that obtained from equation (7), and serves as remarkable evidence for the existence of the energy gap.

Up to now, we have numerically verified that the ground state of $K =$ even shows both ferromagnetic and antiferromagnetic features, and the system is located in the ferrimagnetic phase, while for the $K =$ odd case, the system should be located in the spin liquid phase characterized by a vanishing magnetization. Consequently we believe that our numerical calculations are correct since they are consistent with previous analytical analysis. More importantly, it can be easily found from figures 1–4 that the magnetism for $K =$ even is weakened as the impurity concentration ρ decreases. However, no significant dependence of the magnetic properties on ρ is detected for $K =$ odd.

In addition, we consider the features of the energy gap Δ for different regular dilutions. Unsurprisingly, the energy gap is closed when $K =$ even and it opens again if $K =$ odd, as

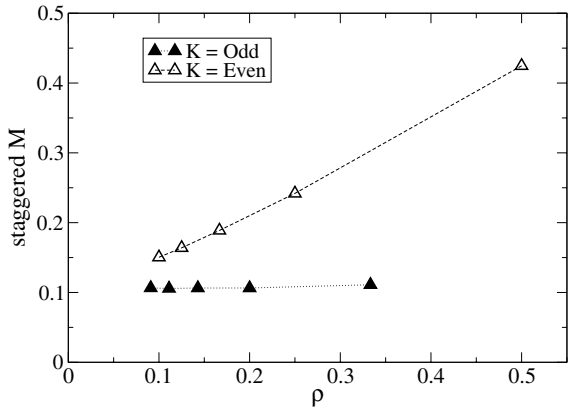

Figure 3. The staggered magnetization versus $\rho = 1/K$ for $\beta = 200$ and $L \sim 200$. The filled triangles present data for $K =$ even and the empty ones, data for $K =$ odd.

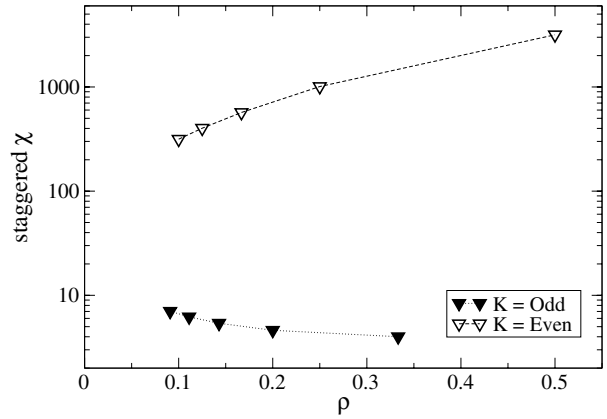

Figure 4. The staggered susceptibility versus $\rho = 1/K$ for $\beta = 200$ and $L \sim 200$. The filled triangles present data for $K =$ even and the empty ones, data for $K =$ odd.

shown in figure 6. The calculations are consistent with the prediction drawn from the non-linear σ model and the LSM theorem [6, 7]. It is interesting to note that the energy gap Δ for $K =$ odd tends to narrow as the $S^1 = 1$ concentration decreases. We confirm the behaviour by fitting Δ to the curve for $1.25\sqrt{\rho}$ in figure 6.

Moreover, we hope to show the finite-size effect of Δ. Although the gap is not exactly closed for $K =$ even due to the finite-size simulations, as shown in figure 7 the gap decays following a $1/L$ power law, and this indicates that the gap will tend to close as $L \to \infty$. For all the $K =$ odd cases, the gap opens stably and almost no finite-size effect is observed.

In order to identify the ground state phases, we perform a calculation of the valence bond solid (VBS) [24] order parameter

$$z \equiv \left\langle \exp\left[\mathrm{i}\frac{2\pi}{L} \sum_{j=1}^{L} j S_j^z \right] \right\rangle. \tag{8}$$

According to the LSM theorem, z vanishes in the gapless phase as the system size $L \to \infty$.

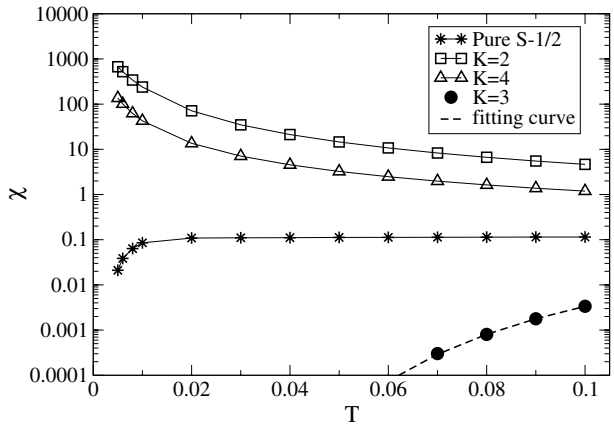

Figure 5. The uniform magnetic susceptibility χ_u versus temperature for size $L \sim 200$. The empty symbols are for $K =$ even and the filled ones, for $K =$ odd. For comparison, the stars present data for the pure $S^2 = 1/2$ AF Heisenberg chain.

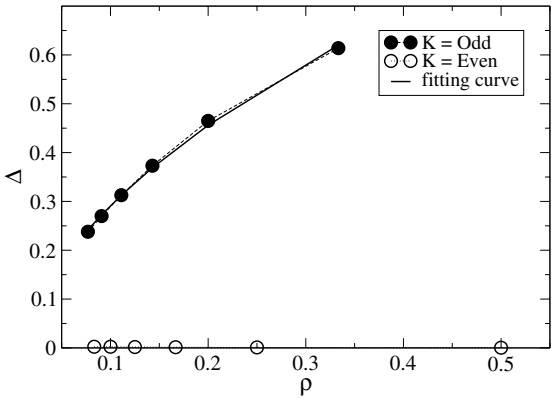

Figure 6. The energy gap versus the diluting parameter $\rho = 1/K$ at $\beta = 200$. The filled circles present data for $K =$ odd and the empty ones, data for $K =$ even. The dashed lines only guide the eyes and the solid line is the fitted curve for $\Delta = 1.25\sqrt{\rho} - 0.1$ with the coefficient of correlation of the curve to the filled circles being 0.999.

On the other hand, one expects z to vary between -1 and $+1$ in a given gapped phase. For exact VBS states, $z = \pm 1$ [25]. Our results are plotted in figure 8. It is clear that $z \approx -1$ for $K =$ odd, indicating that the system is located in a VBS phase, while $z \approx 0$, revealing the gapless energy spectrum, for $K =$ even.

In particular, all these ground state phases can be understood with the scenario of the VBS picture: each impurity $S^1 = 1$ can be regarded as two $\frac{1}{2}$ spins in a triplet state and each of the two $\frac{1}{2}$ spins can form a singlet with their nearest-neighbour $\frac{1}{2}$ spins due to the AF coupling. When $K =$ odd, each unit cell has an even number of $S^2 = \frac{1}{2}$ host spins, and they can fall into singlets with their nearest neighbours including the two $\frac{1}{2}$ spins with $S^1 = 1$ to induce the VBS order shown in figure 9(a). As a result, the system now shows a gapped energy spectrum. But for the case $K =$ even, there are an odd number of $S^2 = \frac{1}{2}$ spins in each unit cell; an active spin which is not used to form a singlet appears, as shown in figure 9(b). Thus there is

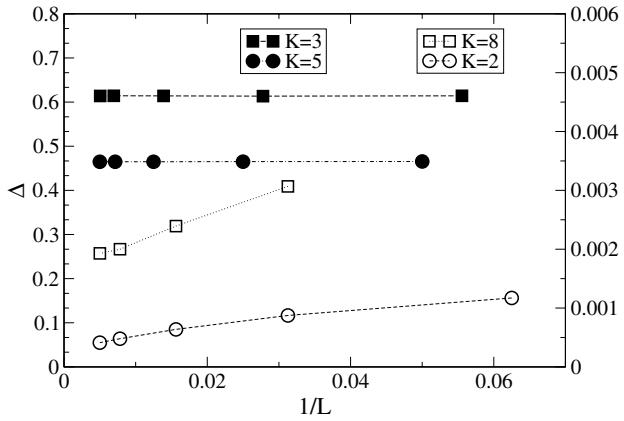

Figure 7. Finite-size effects of the energy gap calculated at $\beta = 200$. The two upper lines of filled symbols present data for $K =$ odd, with the left side y-axis, and the empty symbols, data for $K =$ even, with the right side y-axis.

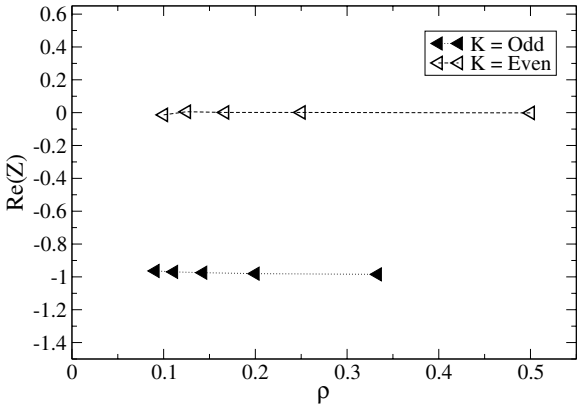

Figure 8. The VBS order parameter z versus the $S^1 = 1$ concentration $\rho 1/K$ for $\beta = 200$ and $L \sim 200$. The filled triangles present data for $K =$ odd and the empty ones, data for $K =$ even.

no VBS order and the spin gap does not emerge. Our results for the VBS order parameter z clearly verify this picture, in figure 8: $z \approx -1$ (0) when $K =$ odd (even). Finally, we note that the VBS phase is stable against the $S^1 = 1$ concentration ρ for $K =$ odd.

3. Discussion and conclusion

Our Monte Carlo simulations confirm that two branches of magnetic states emerge in regular $S^1 = 1$ dilution in $S^2 = 1/2$ host chains. According to the Marshall theorem, the mixed-spin chain with $K =$ even has a ferromagnetic ground state which can be specified by a quantum number $S_{\text{total}} = |S^1 - S^2|N/K$. It is readily observed in figures 1 and 3 that the magnetization per site is finite and decreases linearly to zero as ρ approaches zero, The limit $\rho = 0$ corresponds to the pure $S = \frac{1}{2}$ AF Heisenberg chain with $\mathcal{M} = 0$. For the mixed-spin chain with $K =$ odd, the ground state is a singlet with $S_{\text{total}} = 0$; thus the magnetization per site stays at zero, indicating the non-magnetic behaviour.

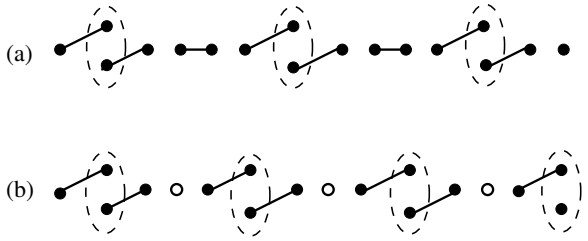

Figure 9. Illustrations of the VBS picture. The dashed ellipses represent $S^1 = 1$, the filled circles are for $S^2 = 1/2$, and the empty circles are for the active $\frac{1}{2}$ spins; (a) for $K =$ odd and (b) for $K =$ even.

Table 1. Comparison of ground state properties of system I and II. $S_{\rm eff}$ denotes the effective spin in a cell, $\langle M\rangle$ ($\langle M_{\rm s}\rangle$) is the uniform (staggered) magnetization, $\chi_{\rm u}$ ($\chi_{\rm s}$) is the uniform (staggered) susceptibility, Δ is the energy gap, and z is the VBS order parameter.

	I: $S^1 = 1$, $S^2 = 1/2$		II: $S^1 = 1/2$, $S^2 = 1$	
	$K =$ odd	$K =$ even	$K =$ odd	$K =$ even
$S_{\rm eff}$	Integer	Half-integer	Half-integer	Half-integer
$\langle M\rangle$	Zero	Finite	Zero	Finite
$\chi_{\rm u}$	Zero	Large	Small	Large
$\langle M_{\rm s}\rangle$	Finite	Finite	Finite	Finite
$\chi_{\rm s}$	Small	Large	Large	Large
Δ	Gapped	Gapless	Gapless	Gapless
z	-1.0	0.0	0.0	0.0

To compare the ground state for $S^1 = 1$ and $S^2 = 1/2$ (system I) reported in this paper with that for $S^1 = 1/2$ and $S^2 = 1$ (system II) in a previous study [18], we collect the main results of the numerical simulations in table 1. One can see that both systems show two different ground state phases, magnetic and non-magnetic. For $K =$ even, the ground state is ferromagnetic for both system I and II, and the magnetization and staggered magnetization are finite and decrease linearly as the impurity concentration ρ approaches zero. However, for the case with $K =$ odd, the VBS order phase appears in system I which has a gapped energy spectrum, but the VBS order is not observed in system II, and the gap vanishes since the spin arrangements cannot induce such an order. These features indicate that the topological order is crucial for the energy gap in the mixed-spin chains. We believe that the fitted relation of the energy gap as a function of the $S^1 = 1$ spin concentration, $\Delta \approx 1.25\sqrt{\rho}$, provides a way to study how the topological order affects the energy gap in such systems.

In conclusion, we have studied the ground state and thermodynamic properties of an $S^1 = 1$ regular dilution in an $S^2 = 1/2$ isotropic antiferromagnetic chain. Our calculations show that there exist different phases in the ground state with respect to the S^1 concentration ρ. When a unit cell of the mixed-spin chain consists of an S^1 impurity and an odd number of host S^2 spins, the ground state is ferromagnetic with a gapless energy spectrum, and the ferromagnetism is gradually weakened as the impurity concentration decreases. When a unit cell consists of an S^1 spin and an even number of S^2 spins, the ground state is the VBS phase, there is a gapped energy spectrum, and the gap gradually approaches zero as ρ decreases. It is interesting that the energy gap can be numerically fitted as $\Delta \approx 1.25\sqrt{\rho}$, and this requires further understanding.

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