Effects of substituting the rare-earth ion R by nonmagnetic impurities in $R_2\text{BaNiO}_5$: Theory and numerical density-matrix renormalization-group results

T.-K. Ng

Department of Physics, Hong Kong University of Science and Technology, Clear Water Bay Road, Kowloon, Hong Kong

Jizhong Lou and Zhao-Bin Su

Institute of Theoretical Physics, P.O. Box 2735, Beijing 100080, People's Republic of China

(Received 10 November 1999; revised manuscript received 25 January 2000)

In this paper we study the effect of substituting R (rare-earth ion) by nonmagnetic ions in the spin-1 chain material $R_2\text{BaNiO}_5$. Using a strong-coupling expansion and numerical density-matrix renormalization-group calculations, we show that spin-wave bound states are formed at the impurity site. Experimental consequences of the bound states are pointed out.

The antiferromagnetic Heisenberg spin chain has been a subject of immense interest since Haldane pointed out that the low-energy physics of integer and half integer spin chains are fundamentally different.¹ With advance in both experiments^{2,3} and numerical techniques,⁴ the prediction by Haldane is now generally accepted. More recently, a series of experiments on the family of quasi-one-dimensional materials with a general formula $R_2\text{BaNiO}_5$,^{3,5-12} where R is one of magnetic rare-earth elements, substituting fully or partially Y have made it possible to study the effect of a staggered magnetic field on a $S=1$ spin chain. The compound Y_2BaNiO_5 is believed to be a good realization of the $S=1$ Haldane gap system.³ The $S=1$ spins are coming from the Ni^{2+} ions. Other members have additional magnetic ions R^{3+} ($R \neq Y$) positioned between two neighboring Ni chains. The coupling between these ions and Ni^{2+} ions are weak. Nevertheless, these magnetic ions are antiferromagnetically ordered below certain Néel temperature T_N , and the ordering affects the Ni chains by providing them an effective background staggered magnetic field. It is expected that the three modes of the Haldane triplet will be splitted by the staggered field at $T < T_N$, with the longitudinal mode energy increases roughly twice as fast as the transverse ones with decreasing temperature below T_N .¹³⁻¹⁶ These effects were indeed observed in neutron-scattering experiments.⁹⁻¹¹

In this paper we shall study the effect of replacing R ions by nonmagnetic impurities. In the case of pure $S=1$ Haldane spin chains, the effect of replacing a spin by a nonmagnetic ion has received much attention because of the theoretical prediction of $S=1/2$ excitations localized at the ends of broken $S=1$ spin chains.¹⁷ The existence of end excitations with fractional spin magnitudes are believed to be a general property of Heisenberg spin chains and is a consequence of the topological properties of these systems.¹⁷ However, the effect of substituting R by nonmagnetic impurities is very different. As far as the Ni^{2+} chain is concerned, the replacement of an R^{3+} ion by a nonmagnetic impurity just alters the local effective (staggered) magnetic field seen by the spin chain, and the topological character of the spin chain is unaffected. Therefore topological $S=1/2$ end excitations are not expected to be induced by the R -ion substitutions. Nev-

ertheless, we shall show in the following that although topological end excitations are not induced by R -ion substitutions, $S=1$ magnon bound states are formed around the impurity and give rise to observable effects on the system.

Our starting point is the effective Hamiltonian for the Ni chain of the $R_2\text{BaNiO}_5$ family at $T < T_N$,

$$H_{bulk} = J \sum_i \vec{S}_i \cdot \vec{S}_{i+1} + h \sum_i (-1)^i S_i^z, \quad (1)$$

where J is the exchange constant, $h = g S \mu_B H_s$ where $H_s \sim M_s$ is the amplitude of the staggered field, and $M_s \neq 0$ at $T < T_N$ is the sublattice magnetization from the R ions. Replacing an R ion by a nonmagnetic impurity at site $i=0$ generates an effective local magnetic field h' . We shall assume a corresponding impurity Hamiltonian

$$H_{im} = h' S_0^z$$

in the following, where $h' = -h$ for a nonmagnetic impurity. We shall consider h' as an arbitrary parameter, and study its effect on the spin chain in the following. The Hamiltonian $H = H_{bulk} + H_{im}$ will be studied using two different approaches. In the first approach, we replace H by the corresponding lattice nonlinear- σ model (or coupled-rotor model),¹⁸ and we shall study the problem in the strong-coupling limit when the Haldane gap m_H is much larger than the coupling between rotors. This approach provides a rather simple physical picture on the effects of staggered magnetic field and impurity on the Haldane chain. The results obtained from the strong-coupling theory is compared with results obtained directly from diagonalizing H with the numerical density-matrix renormalization-group (DMRG) method. Combining the results from the two methods we believe that our study provides a clear picture on the effect of substituting R by nonmagnetic impurities in the $R_2\text{BaNiO}_5$ compound. First we consider the coupled-rotor model.

In this treatment the low-energy physics of an integer Heisenberg spin chain in staggered magnetic field h is described by the Hamiltonian¹⁸

$$H_{rot} = \Delta \sum_i \vec{L}_i \cdot \vec{L}_i - J' \sum_i \vec{n}_i \cdot \vec{n}_{i+1} - h \sum_i n_i^z, \quad (2)$$

where $\vec{n}_i$ is a unit vector located at the link between site $i-1$ and site i , and $\vec{L}_i$ is the angular momentum operator conjugate to $\vec{n}_i$. Δ and J' are parameters to be determined. In the strong-coupling expansion, we assume $\Delta \gg J'$ and treat J' as a small perturbation. In particular, to study the one-magnon excitations, we shall only keep the $l=0,1$ states (l 's are eigenstates of angular momentum operator $\vec{L} \cdot \vec{L}$) and shall diagonalize the Hamiltonian H_{rot} approximately in this subspace. We shall neglect renormalization of ground state by two magnon processes in our theory. First we consider the limit when $h=0$.

After some straightforward algebra, we obtain the effective Hamiltonian in the $l=0,1$ subspace,

$$H_{eff}^{(0)} = \Delta \sum_{i,m} l_i(l_i+1) - \frac{J'}{3} \sum_{i,m} (a_{im}^+ a_{i+1m} + a_{i+1m}^+ a_{im}), \quad (3)$$

where we have set $\hbar=1$. $l(l+1)=0,2$ are the eigenvalues of $\vec{L} \cdot \vec{L}$ in the $l=0,1$ subspace. m is the eigenvalue of l_z , $a_m^+(a_m)$ are raising and lowering operators with matrix elements $\langle 1m | a_m^+ | 00 \rangle = \langle 00 | a_m | 1m \rangle = 1$, and with all other matrix elements equal to zero. $|lm\rangle$ are the angular momentum eigenstates. The one-magnon eigenstates of Eq. (3) are triplets ($l=1, m=0, \pm 1$) with energy spectrum $\epsilon_k = 2[\Delta - (J'/3)\cos(k)]$, and with Haldane gap $m_H = 2(\Delta - J'/3)$.

We now consider the staggered magnetic field h . First we consider the effects of an effective staggered magnetic field h_{eff} on a single rotor. The term $h_{eff} n^z$ couples the $|00\rangle$ and $|10\rangle$ states and the new eigenstates of a single rotor in the $l=0,1$ subspace are

$$|G\rangle = \beta |1,0\rangle + \alpha |0,0\rangle, \quad |0\rangle = -\alpha |1,0\rangle + \beta |0,0\rangle, \quad (4)$$

$$|1\rangle = |1,1\rangle, \quad |-1\rangle = |1,-1\rangle,$$

where $|G\rangle$ is the new ground state, and $|m\rangle (m=0, \pm 1)$ are the new excited states with $l_z=m$. The coefficients α and β are given by

$$\alpha^2 = \frac{1}{2} [1 + \gamma(h_{eff})^{-1}], \quad \beta^2 = \frac{1}{2} [1 - \gamma(h_{eff})^{-1}], \quad (5)$$

where $\gamma(h_{eff}) = \sqrt{(1 + h_{eff}^2/3\Delta^2)}$ and with corresponding eigenenergies $E_G = \Delta[1 - \gamma(h_{eff})]$, $E_0 - E_G = 2\Delta\gamma(h_{eff})$, and $E_{\pm 1} - E_G = \Delta[1 + \gamma(h_{eff})]$. Notice that the energies of the longitudinal ($m=0$) and transverse ($m=\pm 1$) magnon modes are splitted by h_{eff} . The staggered magnetic field also induced a nonzero ground-state expectation value of staggered magnetization, $\langle n_z \rangle = \langle G | n_z | G \rangle = (2/\sqrt{3})\alpha\beta$. To proceed further we replace the rotor Hamiltonian (2) by a mean-field rotor Hamiltonian,

$$H_{rot}^{(MF)} = \Delta \sum_i \vec{L}_i \cdot \vec{L}_i - J' \sum_i \vec{n}_i \cdot \vec{n}_{i+1} - h_{eff} \sum_i n_i^z, \quad (6)$$

where $\vec{n}_i = \langle n_z \rangle + \vec{n}_i'$ and $h_{eff} = h + 2J'\langle n_z \rangle$. Treating the $J'\vec{n}_i' \cdot \vec{n}_{i+1}'$ term as perturbation in the $l=0,1$ subspace as before, we obtain after some straightforward algebra the mean-field equation

$$1 - \frac{h}{h_{eff}} = \frac{4J'}{3\Delta} \gamma(h_{eff})^{-1}, \quad (7)$$

which determines h_{eff} for given h , and with corresponding eigenvalue spectrum for the one magnon states,

$$\epsilon_{\pm 1}(k) = \Delta[1 + \gamma(h_{eff})] - \frac{2J'}{3} \alpha^2 \cos(k),$$

$$\epsilon_0(k) = 2\Delta\gamma(h_{eff}) - \frac{2J'}{3} (\alpha^4 + \beta^4) \cos(k) \quad (8)$$

for the transverse ($m=\pm 1$) and longitudinal ($m=0$) magnons, respectively. At small h , it is easy to show from Eq. (7) that $h_{eff} = h/(1 - 2J'/3\Delta)$, and the system is stable only when $3\Delta > 2J'$, implying that our approximate mean-field treatment is only valid when $m_H > 2J'/3$. It is also easy to show from Eqs. (7) and (8) that the Haldane gaps $m_H^{(m)} (m=0, \pm 1)$ increase as a function of h , with increase in Haldane gap $\Delta m_H^{(0)} \sim 2\Delta m_H^{(\pm 1)}$, in qualitative agreement with experiment and numerical DMRG results.

The impurity Hamiltonian H_{im} generate an extra term in the rotor Hamiltonian,

$$H_{rot}^{(im)} = \frac{(h' - h)}{2} (n_0^z + L_0^z + n_1^z - L_1^z). \quad (9)$$

As a result, the effective staggered magnetic field acting on the spin chain becomes position dependent, with $h(i) = h$ for $i \neq 0,1$, and $h(i) = (h + h')/2$ for $i = 0,1$. Applying a mean-field analysis as before, we obtain new mean-field equations for every site i in the rotor model,

$$J'(\langle n_{i+1}^z \rangle + \langle n_{i-1}^z \rangle) = h_{eff}(i) - h(i),$$

$$\langle n_i^z \rangle = \gamma[h_{eff}(i)] \left(\frac{h_{eff}(i)}{3\Delta} \right), \quad (10)$$

which can be solved numerically. In addition, the $[(h' - h)/2]L^z$ terms in Eq. (10) gives rise to a shift in the energies of the $|m=\pm 1\rangle$ states in the local rotors at sites $i=0,1$ with $E_{\pm 1} - E_G = \Delta[1 + \gamma(h_{eff}(i))] \mp (h' - h)/2\sqrt{3}$.

The effects of impurity magnetic field on the one magnon spectrum can be understood quite easily. The mean-field Eqs. (10) produce effective staggered magnetic field $h_{eff}(i)$'s smaller than h (assuming $h' \sim -h$) within a region of distance $\sim \xi$ around the impurity perturbed sites $i=0,1$, where ξ is the spin-spin correlation length. As a result, the local magnitude of Haldane gap is reduced [see Eq. (8)] in both the longitudinal and transverse channels and induces an attractive potential well of depth $\sim \Delta m_H^{(m)}$ and range $\sim \xi$ for the one magnon states. As a result, bound states of magnon are formed around the impurity. The effective potential well formed around the impurity is stronger in the longitudinal channel than the transverse channel as the effect of h_{eff} on the Haldane gap is about two times larger in the longitudinal channel. Moreover, the energies of the $m=-1$ magnon

FIG. 1. The low-energy spectrum in the presence of single impurity as a function of h' obtained in our mean-field theory with $\Delta=1$, $J'=1.47$, and $h=0.2$.

states become lower than the $m=1$ states because of the additional $-(h'-h)/2L^z$ coupling in $H_{rot}^{(im)}$. In Fig. 1 we show the low-energy spectrum obtained in our theory with $\Delta=1$, $J'=1.47$, $h=0.2$ as a function of h' . Notice that in the presence of single impurity, the translational symmetry of the Hamiltonian is broken and the only symmetry left is the reflection symmetry upon the impurity site. As a result, the low-energy one magnon spectrum of the system can be divided into six sectors labeled by $(S_{tot}^z)^{parity} = 0^+, 0^-, 1^+, 1^-, (-1)^+, (-1)^-$, respectively, where S_{tot}^z ($=m$) is the z component of total spin, and $+$ or $-$ denotes the parity of the wave functions. We see from the energy spectrum that spin-wave bound state develops when $h' < 0.2$, and there is roughly one bound state (except the -1^+ magnons at intermediate value of h') per sector.

To test our theory and to get more quantitative predictions of the impurity effect we also carry out explicit DMRG calculations for the low-energy spectrum of Hamiltonian $H = H_{bulk} + H_{im}$. We use the standard DMRG algorithm^{19,20} by targeting four states and keeping 400 optimal states, and have studied chains with length up to $L=100$. We have fixed $h=0.2(J)$ in our calculation, which seems to be an appropriate value for the $R_2\text{BaNiO}_5$ chains.¹⁵ The value of h' is varied to study the effect of impurity on the low-energy spectrum. The numerical results of the low-energy magnon spectrum in the six $(S_{tot}^z)^{parity}$ sectors are shown in Fig. 2. Our results show that in the four sectors 1^+ , 1^- , $(-1)^-$, $(-1)^+$ corresponding to the transverse modes, one bound state is induced in each sector when $h' < 0.2$, in agreement with our mean-field theory. The behavior of the bound-state energy as a function of h' is also qualitatively similar to

FIG. 2. The low-energy excitation states of the six sectors for staggered magnetic field $h=0.2$ and chain length $L=100$; the dotted line is the corresponding value of the Haldane gap for $h=0.2$ without impurity.

those obtained in mean-field theory. In the 0^+ and 0^- sectors which correspond to longitudinal modes, the situation is more complicated. We find that more than one bound states emerge inside the Haldane gap in contrast to mean-field theory. Notice that although the number of bound states differs, the qualitative behavior of the lowest bound-state energies as a function of h' in the 0^+ and 0^- sectors are qualitatively similar to mean-field results.

The reason why there exists only one bound state in mean-field theory can be understood quite easily. Our mean-

FIG. 3. The chain length dependence of the lowest nine energy levels for 0^+ sector for $h=0.2$ and $h'=-1.0$; the dotted line is the gap value at the thermodynamical limit.

FIG. 4. The magnetization density difference of the lowest excitation state of each sector to the ground state, $\langle S_i^z \rangle_{l.e.} - \langle S_i^z \rangle_{g.s.}$ at the physical regime $h' = -0.2$.

field theory is valid only when $m_H > 2J'/3$, corresponding to correlation length $\xi \sim 1$ lattice site whereas $\xi \sim 6$ lattice sites in real spin-one chains. The size of the effective attractive potential well is of order ~ 2 lattice sites in our theory, which is much smaller than the size of the effective attractive potential well (~ 12 lattice sites) in real spin-one chains. It is therefore not surprising that the number of bound states in real spin-one chains is larger than one per sector but there exists only one bound state per sector in our mean-field theory.

To determine the number of the bound states in the longitudinal sectors, we carried out a more detailed calculation for 0^+ sector by targeting ten states and keeping 800 optimal states for $h' = -1.0$ and $h = 0.2$, the chain length dependence of these states are shown in Fig. 3. We see from the figure that as the length of the chain increases, more in-gap bound states are formed. In fact, it is difficult to determine from our numerical result the exact number of bound states in this sector.

In the physical regime $h' = -0.2$ which corresponds to nonmagnetic impurity, we find that bound states exist in the 0^+ , 0^- , 1^+ , and $(-1)^+$ sectors. The bound-state energies in the 0^+ and $(-1)^+$ sectors are larger and are roughly $0.1 \times m_H$, where m_H are the corresponding Haldane gap energies, whereas the bound-state energies in the 0^- and 1^+ sectors are much smaller ($\sim 0.02 \times m_H$). The existence of bound states at $h' = -0.2$ can be seen more clearly from the magnetization density difference $\langle S_i^z \rangle_{l.e.} - \langle S_i^z \rangle_{g.s.}$ as a function of position i , which measures the magnetization carried by the lowest excited state at each sector. The results are shown in Fig. 4. We can see clearly from the figures that the first excited states of 0^+ , 0^- , 1^+ , and $(-1)^+$ sectors are bound magnon states whereas the first excited states of the 1^- and $(-1)^-$ sectors are bulk states.

The bound states can be observed in neutron-scattering experiments on high quality crystals as an effective reduction of Haldane gap by $\sim 10\%$ at $T < T_N$ when nonmagnetic impurities are introduced. They also show up as extra spectral weights with energy $\sim 0.9m_H$ in dynamic structure factor $S(q, \omega)$ at wave vectors q away from π .

In summary, we have studied the effect of substituting R (rare-earth ion) by nonmagnetic ions in the spin-one chain material $R_2\text{BaNiO}_5$. We find in numerical DMRG calculation that magnon bound states appear at the impurity site. The bound states can be qualitatively understood by a mean-field strong-coupling expansion treatment of the spin chain and can be observed in neutron scattering experiments.

This work was supported by the HKUGC under RGC Grant No. HKUST6143/97P and by Chinese Natural Science Foundation. J. Lou would like to thank Dr. Shaojin Qin and Dr. Tao Xiang for useful discussion.

¹F. D. M. Haldane, Phys. Lett. **93A**, 464 (1983); Phys. Rev. Lett. **50**, 1153 (1983).

²M. Chiba *et al.*, Phys. Rev. B **44**, 2838 (1991); G. E. Granroth, M. W. Meisel, M. Chaparala, Th. Jolicoeur, B. H. Ward, and D. R. Talham, Phys. Rev. Lett. **77**, 1616 (1996).

³Guangyong Xu, J. F. DiTusa, T. Ito, K. Oka, H. Takagi, C. Broholm, and G. Aeppli, Phys. Rev. B **54**, R6827 (1996).

⁴S. R. White and D. A. Huse, Phys. Rev. B **48**, 3844 (1993); O. Golinelli, Th. Jolicoeur, and R. Lacaze, *ibid.* **50**, 3037 (1994); S. Qin, X. Wang, and Lu Yu, *ibid.* **56**, 14 251 (1997); X. Wang, S. Qin, and Lu Yu, *ibid.* **60**, 14 529 (1999).

⁵V. Sachan, D. J. Buttrey, J. M. Tranquada, and G. Shirane, Phys. Rev. B **49**, 9658 (1994).

⁶A. Zheludev, J. M. Tranquada, T. Vogt, and D. J. Buttrey, Europhys. Lett. **35**, 385 (1996); Phys. Rev. B **54**, 6437 (1996).

⁷A. Zheludev, J. M. Tranquada, T. Vogt, and D. J. Buttrey, Phys. Rev. B **54**, 7210 (1996).

⁸A. Zheludev, J. P. Hill, and D. J. Buttrey, Phys. Rev. B **54**, 7216 (1996).

⁹T. Yokoo, A. Zheludev, M. Nakamura, and J. Akimitsu, Phys. Rev. B **55**, 11 516 (1997).

¹⁰T. Yokoo, S. Raymond, A. Zheludev, S. Maslov, E. Ressouche, I. Zaliznyak, R. Erwin, M. Nakamura, and J. Akimitsu, Phys. Rev. B **58**, 14 424 (1998).

¹¹A. Zheludev, E. Ressouche, S. Maslov, T. Yokoo, S. Raymond, and J. Akimitsu, Phys. Rev. Lett. **80**, 3630 (1998).

¹²S. Raymond, T. Yokoo, A. Zheludev, S. E. Nagler, A. Wildes, and J. Akimitsu, Phys. Rev. Lett. **82**, 2382 (1999).

¹³S. Maslov and A. Zheludev, Phys. Rev. B **57**, 68 (1998).

¹⁴S. Maslov and A. Zheludev, Phys. Rev. Lett. **80**, 5786 (1998).

¹⁵Jizhong Lou, Xi Dai, Shaojin Qin, Zhaobin Su, and Lu Yu, Phys. Rev. B **60**, 52 (1999).

¹⁶Indrani Bose and Emily Chattopadhyay, Phys. Rev. B **60**, 12 138 (1999).

¹⁷T. K. Ng, Phys. Rev. B **50**, 555 (1994).

¹⁸S. Chakravarty, B. I. Halperin, and D. R. Nelson, Phys. Rev. B **39**, 2344 (1989).

¹⁹S. R. White and R. M. Noack, Phys. Rev. Lett. **68**, 3487 (1992);
S. R. White, *ibid.* **69**, 2863 (1992); Phys. Rev. B **48**, 10 345

(1993).

²⁰For a review, see *Density Matrix Renormalization*, edited by I. Peschel, X. Wang, M. Kaulke, and K. Hallberg, Lecture Notes in Physics Vol. 528 (Springer, Berlin, 1999).