

Spin Dynamics of Hole Doped $Y_{2-x}Ca_xBaNiO_5$

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(Received 14 August 1995)

We propose an electronic model for the recently discovered hole doped compound $Y_{2-x}Ca_xBaNiO_5$. From a multiband Hamiltonian with oxygen and nickel orbitals, a one band model is discussed. Holes are described using Zhang-Rice-like $S = \frac{1}{2}$ states at the nickels propagating on a $S = 1$ spin chain. Using numerical techniques to calculate the dynamical spin structure factor $S(q, \omega)$ in a realistic regime of couplings, spectral weight in the Haldane gap is observed in agreement with neutron scattering data. The case of static defects relevant for Zn-doped chains is also discussed. Ferromagnetic states at high hole mobility are favored in our model, contrary to what occurs in the 1D t - J model.

PACS numbers: 75.25.+z, 75.10.Jm, 75.50.Ee

Spin-liquid ground states in Heisenberg $S = 1$ chains and $S = \frac{1}{2}$ ladders have been studied theoretically as paradigms of disordered nonclassical systems [1,2]. These spin models can be physically realized in several compounds. An important issue is the effect of hole doping on these systems. Theoretical studies of doped $S = \frac{1}{2}$ ladders have shown that the spin gap survives in the presence of holes, and that the spin-gapped phase is favorable for superconductivity [2]. Behavior indicating a spin gap has also been observed experimentally in some underdoped high- T_c cuprates. However, the case of the doped $S = 1$ chains has been considered only very recently in the context of the $S = 1$ metal oxide Y_2BaNiO_5 [3]. Lightly doping this compound with Ca introduces hole carriers in the chains. Two remarkable experimental features were observed upon doping, namely, (i) the reduction of the resistivity ρ_{dc} by several orders of magnitude, and (ii) the creation of states inside the Haldane gap as revealed by inelastic neutron scattering (INS) data [4].

To understand these in-gap states, *spin* systems with site or bond impurities have been recently proposed [5]. Holes are assumed to be so strongly localized that their mobility is neglected. In a more recent approach, dynamics was provided to the holes [6] but the Ni-Ni exchange J was assumed larger than both the hole hopping amplitude and the short-bond NiO exchange, which is unrealistic. While studying these limits is instructive since gap states are produced, the drastic reduction in ρ_{dc} observed experimentally upon doping [4] suggests that holes may be mobile over lengths of several lattice spacings. Thus here we propose a new model for $Y_{2-x}Ca_xBaNiO_5$ with fully *mobile* $S = \frac{1}{2}$ holes interacting with $S = 1$ spins, which is studied using realistic couplings.

In Ni^{2+} surrounded by oxygens, $d_{3z^2-r^2}$ and $d_{x^2-y^2}$ are the two active orbitals [7]. Then, as a Hamiltonian for the Ni-O chains in the hole notation we propose

$$H = - \sum_{\langle ij \rangle, \sigma, \alpha} t_{pd\alpha} (d_{i\sigma\alpha}^\dagger p_{j\sigma} + \text{h.c.}) + U_d \sum_{i, \alpha} n_{i\uparrow}^\alpha n_{i\downarrow}^\alpha + U_p \sum_j n_{j\uparrow} n_{j\downarrow} + \Delta \sum_j n_j - |J_{\text{Hund}}| \sum_i \mathbf{S}_{i1} \cdot \mathbf{S}_{i2}. \quad (1)$$

i (j) denotes Ni (O) sites. $\alpha = 1$ (2) corresponds to the Ni orbitals $d_{3z^2-r^2}$ ($d_{x^2-y^2}$). The Coulomb repulsion is U_d (U_p) at the Ni (O) sites, and Δ is the charge-transfer energy. $d_{i\sigma\alpha}$ are *hole* operators corresponding to a Ni site, spin σ and orbital α , while $p_{j\sigma}$ are O-hole operators. The last term in Eq. (1) is a *ferromagnetic* coupling between the Ni holes on different orbitals (using $\mathbf{S}_{i\alpha} = d_{i\alpha}^\dagger \sigma d_{i\alpha} / 2$), which enforces Hund's rule. This term is important to produce the expected $S = 1$ state in Ni^{2+} . From an analysis of $Li_xNi_{1-x}O$, it was found that $\Delta = 6.0$ eV, $U_d = 9.5$ eV, and $U_p = 4.6$ eV [8]. Since $U_d > \Delta$ then the compound is in the charge-transfer regime [9]. J_{Hund} is obtained from a $(NiO)^{10-}$ cluster [10] where the energy difference ($|J_{\text{Hund}}|$) between the $S = 1^3A$ and the $S = 0^1E$ levels is 1.3 eV. The hopping amplitudes are $t_{pd1} = 1.3$ eV and $t_{pd2} = 0.75$, according to a cluster calculation [11,12].

The study of mobile holes in model Eq. (1) is a difficult task since the energy scale is eV, while the interesting physics for Y_2BaNiO_5 occurs at the J scale of about 30 meV. Thus we need to construct an effective low-energy Hamiltonian from Eq. (1) as Zhang and Rice did in their reduction of the 2D multiband Hubbard model to the t - J model [13]. In $Y_{2-x}Ca_xBaNiO_5$ holes populate oxygens [4], and they have a strong exchange J' with neighboring Ni. This may lead to low-energy states with $S = \frac{1}{2}$ or $S = \frac{3}{2}$, after the oxygen $S = \frac{1}{2}$ hole mixes with neighboring $S = 1$ spins. To study this effect, we solved a small cluster O-Ni-O described by Eq. (1) in the three-hole subspace (two of them producing the Ni $S = 1$, and the other providing an extra oxygen hole). From the spectrum, and using the parameters given before,

we indeed found a $S = \frac{1}{2}$ ground state, with the $S = \frac{3}{2}$ state located ~ 1.3 eV higher. This energy difference is robust even if the parameters of Eq. (1) are modified within acceptable windows to account for experimental uncertainties. Next, to proceed à la Zhang-Rice we should construct a basis of orthogonal Wannier orbitals from the doublet ground state of the three-hole O-Ni-O cluster, and from it derive a t - J -like model. Although we have not done this explicitly [14], it is intuitively clear that the effective model will be dominated by states centered *only* at the Ni sites which can be $S = 1$ (“spins”) or $S = \frac{1}{2}$ (“holes”) [15]. Thus in our model the study of carriers on $Y_{2-x}Ca_xBaNiO_5$ amounts to the analysis of $S = \frac{1}{2}$ hole-like states in an $S = 1$ background [16]. Note that recent μ SR data indeed show that the carriers have $S = \frac{1}{2}$ [17].

To obtain the allowed hole hopping processes it is important to remember the composite character of the $S = \frac{1}{2}$ hole state. To guide the intuition a graphical representation is useful [Fig. 1(a)]. The low-energy states with $S = 1$ and $\frac{1}{2}$ located on nearest-neighbor (NN) Ni sites are actually represented as five holes (four in the Ni d shells and one in the O p shell) on a Ni-O-Ni cluster. The dashed line signals a possible singlet between the O hole and one of the Ni holes, producing a $S = \frac{1}{2}$ state as was described before. However, it is clear that the Ni partner of the oxygen hole can be easily switched from right to left producing an effective hopping process of the $S = \frac{1}{2}$ low-energy state as shown in Fig. 1(a). Other hoppings do not correspond to a mere interchange of the states, but a spin flip can also occur. Exploring all possibilities, it can be shown that the allowed processes are those listed in Fig. 1(b) (plus their spin reversed analogs). These hopping terms have also been derived by Zaanen and Oles [18] using more formal arguments in their complementary analysis of triplet holes moving in a $S = \frac{1}{2}$ background.

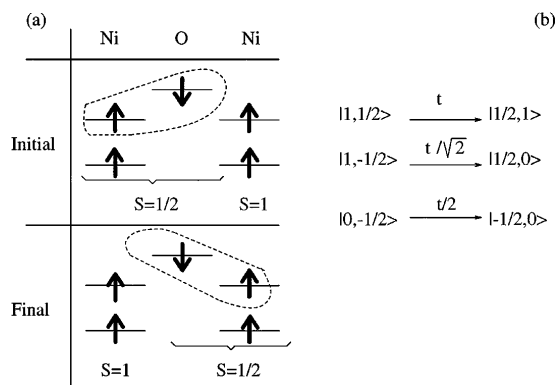


FIG. 1. (a) Graphical representation of a hopping process as explained in the text; (b) Allowed hopping processes in model Eq. (2). The numbers in the ket represent the z projection of the $S = 1$ and $\frac{1}{2}$ spin states of Eq. (2) at two arbitrary sites i and j , respectively. P_{ij} in Eq. (2) enforces the *absence* of the hopping $|1, -1/2\rangle \rightarrow |-1/2, 1\rangle$. The spin projections *only* change by $1/2$ or $-1/2$ at each site.

Thus based on the diagonalization of the O-Ni-O cluster, symmetry considerations, and assuming that the dominant hopping process is between NN Ni sites, we arrive at a one-band Hamiltonian:

$$H = J \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j - t \sum_{\langle ij \rangle} P_{ij} (\hat{S}_i \cdot \hat{S}_j + \frac{1}{2}). \quad (2)$$

The first term is the Heisenberg interaction arising from Eq. (1) at half-filling and strong coupling. It only affects the $S = 1$ spins. Calculating J directly from Eq. (1) is difficult, and thus here we simply take the exchange from experiments, i.e., $J = 0.03$ eV. The second term in Eq. (2) is explicitly rotationally invariant and it acts only when spins 1 and $\frac{1}{2}$ share a link. P_{ij} simply permutes the two spins. The notation $\hat{S}_i = (\hat{S}_x, \hat{S}_y, \hat{S}_z)$ is used in the hopping term to indicate that this spin operator can act over both $S = 1$ and $\frac{1}{2}$ states depending on what spin is located at site i . Their action is the standard for a spin operator. For example, $\hat{S}_i^- \hat{S}_j^+ |m_i^z = 1, m_j^z = -\frac{1}{2}\rangle = \sqrt{2} |m_i^z = 0, m_j^z = +\frac{1}{2}\rangle$. It is natural to assume that the realistic coupling regime is $t > J$ although we have not derived t and J from Eq. (1) [19]. Note that the Wannier orbitals used in Refs. [13,14] will be more spread in 1D than in 2D, and this implies that next-nearest-neighbor (NNN) hopping processes are more important in our NiO model than in the 2D t - J model. However, there is no reason to expect that the qualitative features of the model will change with the addition of NNN hole hoppings, and thus we neglect these terms here. Only when accurate photoemission experiments become available might the relevance of NNN hoppings become important for a quantitative description of the hole dispersion. Note also that the hopping term in Eq. (2) is formally written like the hopping reported in Ref. [6]. This is simply due to rotational invariance. The Hamiltonian of Ref. [6] contains both O and Ni orbitals, with a phenomenological direct O-O hopping, which makes their approach similar to “spin-fermion” models for the cuprates. Our scenario, however, is similar to the “ t - J ” family of high- T_c theories.

An accurate analysis of 1D Hamiltonians like Eq. (2) can be done using exact diagonalization (ED) techniques [20,21]. With this method, we first calculated the dispersion of *one* hole $\epsilon(q)$, using model Eq. (2) [see Fig. 2(a)]. $\epsilon(q)$ is not symmetric with respect to $\pi/2$, contrary to systems with antiferromagnetic order. The minimum q_{\min} at $t/J = 2.0$ is at $\pi/3$ for the chain used in Fig. 2(a). In the bulk limit we expect that q_{\min} will move with continuity as a function of t/J . While the hole ground state at most q values has $S = \frac{1}{2}$, the states close to $q = \pi$ have $S = \frac{3}{2}$, i.e., the band in Fig. 2(a) is actually made out of two energy levels with different spins. In the range $0.5 \leq t/J \leq 4.0$, the bandwidth W is approximately $(0.2-0.3)J$ [Fig. 2(b)], i.e., much smaller than the $W \sim 2J$ reported for holes in 2D $S = \frac{1}{2}$ antiferromagnets [20]. Several of these features could be observed in angle-resolved photoemission experiments. The peculiar dynamics of Eq. (2) is responsible for the abnormally small W . Such a large

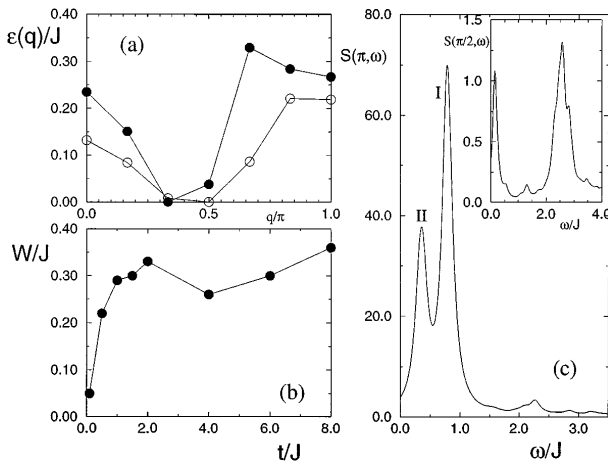


FIG. 2. (a) $\epsilon(q)$ on an $N = 12$ chain with one hole and periodic boundary conditions (PBC) using Eq. (2). The energy is measured with respect to the lowest-energy state. Open (full) circles correspond to $t/J = 0.5$ (2.0). (b) Hole bandwidth W [energy difference between the highest and lowest energy in $\epsilon(q)$] vs t/J on the $N = 12$ chain. (c) $S(\pi, \omega)$ of model Eq. (2) with $t/J = 2.0$, $N = 12$, one hole and PBC. The meaning of peaks I and II is discussed in the text. In the inset $S(\pi/2, \omega)$ is shown for the same set of parameters.

effective mass increases the tendency to hole localization, providing a natural explanation for the lack of true metallicity in $Y_{2-x}Ca_xBaNiO_5$ and in doped 2D nickelates.

Figure 2(c) shows the dynamical spin structure factor $S(\pi, \omega)$ at a nominal hole density $x = \frac{1}{12} \sim 0.083$ and $t/J = 2.0$ calculated with ED [22] (in the computation of this quantity the spin-flop operator affects both the $S = 1$ and $S = \frac{1}{2}$ degrees of freedom). The qualitative agreement with the INS data reported for $Y_{2-x}Ca_xBaNiO_5$ [4] at $x \sim 0.04-0.10$ is clear [23]. The spectrum shows two main features: peak I caused by spin excitations in the $S = 1$ chain away from the hole, and peak II induced by the addition of a $S = \frac{1}{2}$ hole. To justify these identifications, let us study the q dependence of peaks I and II [Fig. 3(a)]. Since $S(q, \omega)$ at finite x has fine structure in energy in addition to the two main peaks [see inset of Fig. 2(c)], the results shown in Fig. 3(a) are just rough estimations, but we believe the main qualitative features are robust. Clearly peak I follows closely the position of the one-magnon excitation observed in undoped $S = 1$ chains, while peak II is virtually dispersionless. Both peaks rapidly lose intensity when moving away from π , in agreement with INS [4] results where only $q = \pi$ provided a large signal for the hole-induced band [24].

Since INS experiments have been carried out also with zinc doping [4], which only provides defects to the chains but not carriers, it is important to study $S(q, \omega)$ for a Heisenberg chain with *open* boundary conditions [Fig. 3(b)]. At the ends of the chain, it is well known that extended $S = \frac{1}{2}$ states are formed which are coupled forming singlets (S) and triplets (T), becoming degenerate as $N \rightarrow \infty$. These states are best understood using the valence bond theory of Refs. [25,26]. Peak II in Fig. 3(b)

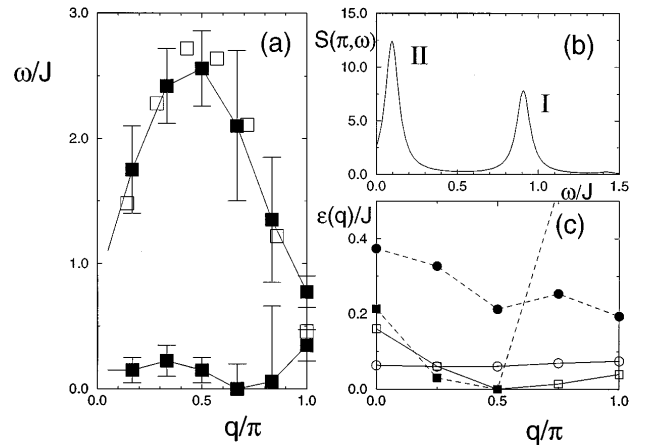


FIG. 3. (a) Energy of the excitation with the highest intensity in $S(q, \omega)$ [parameters as in Fig. 2(c)]. The full squares denote peaks I and II as they evolve with q , with the error bars representing their width. The open squares are the one-magnon peak position on a $N = 14$ undoped $S = 1$ Heisenberg model with PBC. (b) $S(\pi, \omega)$ for the undoped $S = 1$ Heisenberg model on a 12 sites chain with OBC. The meaning of the peaks is discussed in the text. (c) Energy vs q of the relevant low-energy states (8 sites chain with PBC and one hole). Open squares and circles denote the states with $S = \frac{1}{2}$ and $\frac{3}{2}$, respectively, discussed in the text at $t/J = 0.2$. Full squares and circles correspond to the same $S = \frac{1}{2}$ and $\frac{3}{2}$ states, respectively, but in the realistic regime of $t/J = 2.0$.

corresponds to the transition between the S and T states (we explicitly checked that the main contribution to peak II in Fig. 3(b) comes from spins located near the *ends* of the $S = 1$ chain). Note that in Fig. 3(b) it seems strange that the strength of peak II is relatively large since it should vanish in the bulk recovering the Haldane gap $\sim 0.4J$ (peak I). We believe the reason is that the “size” of the $S = \frac{1}{2}$ end states is ~ 6 lattice spacings [26] and thus only when $N \gg 12$ (or the density of hole defects is $x \ll 1/12$) will the contribution of the S - T transition be negligible. This leads us to predict that for *zinc* doping $y \sim 0.10$, substantial weight inside the Haldane gap should be observed with neutron scattering as for the case of *Ca* doping (experiments thus far have been done only for $y = 0.04$ [4]).

To understand the results of Fig. 2(c), it is likely that we need the low-energy end states of the severed Ni chain in combination with the $S = \frac{1}{2}$ hole. Recently, Penc and Shiba [6] emphasized this point to describe the physics of a $S = \frac{1}{2}$ hole at an O between Ni’s in the low mobility regime $t \ll J$ of their multiband model. We believe a similar reasoning can be applied for the $S = \frac{1}{2}$ Zhang-Rice doublet between nickels. For a ring with N *even*, the end states of the spin chain are in a triplet state separated by a small gap from the singlet [27]. This triplet couples to the $S = \frac{1}{2}$ hole forming $S = \frac{1}{2}$ and $\frac{3}{2}$ states, split by a nonzero t/J [28]. For low-mobility holes the $S = \frac{1}{2}$ state has the lowest energy [6], as in Fig. 3(c) at $t/J = 0.1$. It is remarkable that increasing t/J to realistic values

(highly-mobile holes) we have here observed that the energy difference between these states remains a fraction of J [see Fig. 3(c) at $t/J = 2.0$].

Finally, note that as t/J increases further, the kinetic energy becomes dominant and the hole prefers to be surrounded by a cloud of ferromagnetically aligned spins. On the $N = 12$ chain, the hole state with $S = \frac{3}{2}$ becomes the ground state at $t/J \sim 5.74$. Although this coupling is not unrealistic, μ SR results indicate $S = \frac{1}{2}$ holes in the actual NiO doped chains [17], and thus phenomenologically we should work in the regime $t/J < 5.74$. Nevertheless, it is interesting that model Eq. (2) tends to favor ground state ferromagnetism contrary to what occurs in the 1D t - J model. We also found that studying *two* holes on a ten-site chain (density $x = \frac{2}{10} \sim 0.20$), the Haldane gap remnants are difficult to identify in $S(q, \omega)$. This prediction can be tested experimentally by increasing x in $Y_{2-x}Ca_xBaNiO_5$ beyond the current limit $x = 0.10$.

Summarizing, a model for *mobile* carriers in NiO chains was here proposed. $S(q, \omega)$ shows states in the Haldane gap in agreement with neutron scattering data. We believe that theories where holes are modeled as spin impurities can be distinguished from the dynamical holes approach described here by measuring the optical conductivity. The present theory would predict a substantial weight inside the charge transfer gap upon doping since holes are highly mobile and finite ω precursors of Drude peaks should appear in severed NiO chains. Finally note that the variable-range-hopping behavior (not a clean metal) observed in the resistivity measurements [4] may be due to the relevance of a small amount of impurities in 1D systems. We expect that our Hamiltonian will reproduce features of the NiO doped chains tested at finite energies and length scales where holes seem delocalized. The combined effect of interaction and disorder in the system studied here certainly deserves further work.

We thank G. Zimanyi, J. Zaanen, A. Fujimori, J. DiTusa, G. Aeppli, N. Bonesteel, H. Eisaki, and V. Dobrosavljevic for useful conversations. This work was supported by ONR under Grant No. N00014-93-0495, and also by the NHMFL and Martech (FSU).

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- [1] F.D. Haldane, Phys. Rev. Lett. **50**, 1153 (1983).
 [2] E. Dagotto, J. Riera, and D. J. Scalapino, Phys. Rev. B **45**, 5744 (1992); E. Dagotto and T. M. Rice (to be published).
 [3] B. Batlogg, S-W. Cheong, and L. W. Rupp, Jr., Physica (Amsterdam) **194B-196B**, 173 (1994); A. P. Ramirez *et al.*, Phys. Rev. Lett. **72**, 3108 (1994).
 [4] J. F. DiTusa *et al.*, Phys. Rev. Lett. **73**, 1857 (1994).
 [5] Z.-Y. Lu, Z.-B. Su, and Lu Yu, Phys. Rev. Lett. **74**, 4297 (1995); E. Sorensen and I. Affleck (to be published); S. Fujimoto and N. Kawakami (to be published).
 [6] K. Penc and H. Shiba, Phys. Rev. B **52**, R715 (1995).
 [7] The Jahn-Teller induced splitting will be neglected here.
 [8] P. Kuiper *et al.*, Phys. Rev. Lett. **62**, 221 (1989); H. Eisaki *et al.*, Phys. Rev. B **45**, 12513 (1992).

- [9] J. Zaanen *et al.*, Phys. Rev. Lett. **55**, 418 (1985).
 [10] M. E. Lines, Phys. Rev. **164**, 736 (1967) (see Fig. 2). Although $KNiF_3$ is studied, with Ni surrounded by F, the energy levels of Ni^{2+} do not change much in an oxygen cage [A. Fujimori (private communication)].
 [11] J. van Elp *et al.*, Phys. Rev. B **45**, 1612 (1992); J. Bala, A. Oleś, and J. Zaanen, Phys. Rev. Lett. **72**, 2600 (1994).
 [12] This is in agreement with estimations using $t_{pd} \approx -22.69 \text{ eV } \text{\AA}^2 r_d^{3/2} / d^{7/2}$ [W. A. Harrison, *Electronic Structure and the Properties of Solids* (Dover Publications, Inc., New York, 1980)] where $r_d = 0.71 \text{ \AA}$ is a typical d -orbital size in Ni^{2+} and $d = 1.885 \text{ \AA}$ is the Ni-O distance in Y_2BaNiO_5 (Ref. [3]). This approach gives $t_{pd} \approx 1.5 \text{ eV}$.
 [13] F. Zhang and T. M. Rice, Phys. Rev. B **37**, 3759 (1988).
 [14] For additional details on the derivation of the t - J model from the multiband model, see F. C. Zhang, Phys. Rev. B **39**, 7375 (1989); J. J. Jefferson *et al.*, *ibid.* **45**, 7959 (1992); A. A. Aligia *et al.*, *ibid.* **49**, 13061 (1994); V. I. Belinicher and A. L. Chernyshev *ibid.* **49**, 9746 (1994); and references therein. The detailed derivation of the one band from the multiband model in the present paper remains to be addressed in the future.
 [15] Similar ideas were proposed by Bala, Oleś, and Zaanen (Ref. [11]) in computing photoemission intensities for NiO.
 [16] However, note that the competition between $S = \frac{1}{2}$ and $S = \frac{3}{2}$ is controversial. See van Elp *et al.* [11] and A. Fujimori and F. Minami, Phys. Rev. B **30**, 957 (1984).
 [17] K. Kojima *et al.*, Phys. Rev. Lett. **74**, 3471 (1995).
 [18] J. Zaanen and A. Oleś, Phys. Rev. B **48**, 7197 (1993); J. Zaanen, A. Oleś, and P. Horsch, *ibid.* **46**, 5798 (1992).
 [19] A Heisenberg interaction $J_{1-1/2}$ ($J_{1/2-1/2}$) between one $S = 1$ and a hole (two holes) is here neglected.
 [20] E. Dagotto, Rev. Mod. Phys. **66**, 763 (1994).
 [21] We have found that Monte Carlo techniques for Eq. (2) have sign problems even in 1D.
 [22] Note that the one-hole ground state has a finite momentum, as shown in Fig. 2(a), which complicated that analysis of $S(q, \omega)$. However, we believe the main results shown in this paper are not affected by this detail. A study of two holes on a 24 site chain is not possible numerically.
 [23] The internal structure of the Zhang-Rice $S = \frac{1}{2}$ doublet will become noticeable in INS only at energies where the $S = \frac{3}{2}$ excited state of the O-Ni-O cluster is reached.
 [24] While peak II in Fig. 2(c) seems sharply located at about half the Haldane gap, the experimental situation may correspond to a random average of severed chains with different lengths including $N < 12$ where the energy of peak II is modified by size effects. This smears the low-energy peak improving the agreement with experiments.
 [25] I. Affleck *et al.*, Commun. Math. Phys. **115**, 477 (1988).
 [26] S. Miyashita and S. Yamamoto, Phys. Rev. B **48**, 913 (1993).
 [27] If N is *odd*, the singlet spin configuration of the end states of the chain coupled to the $S = \frac{1}{2}$ hole also has a $S = \frac{1}{2}$ state as the ground state, and the reasoning is similar.
 [28] The singlet state made out of the end states of the severed chain forms a $S = \frac{1}{2}$ state with the hole, which is located at a higher energy.