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

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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 derived. Holes are described using Zhang-Rice-like $S=1/2$ states at the nickel 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. Low energy states with $S=3/2$ appear in the model. Several predictions are made to test these ideas.

75.25.+z, 75.50.Ee, 75.10.Jm

Spin-liquid ground states in Heisenberg $S=1$ chains and $S=1/2$ ladders have been studied theoretically as paradigms of disordered nonclassical systems. 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 $S=1/2$ ladders have shown that the spin gap survives in the presence of holes, and that the spin-gapped phase is favorable for superconductivity. Behavior indicating a spin gap has also been observed experimentally in some underdoped high-Tc cuprates. However, the case of the doped metal oxide $Y_{2}BaNiO_{5}$ has also been observed experimentally in some underdoped high-Tc cuprates. Theoretical studies of doped $S=1/2$ ladders have shown that the spin gap survives in the presence of holes, and that the spin-gapped phase is favorable for superconductivity. In Ni$^{++}$ surrounded by oxygens, $d_{3z^2-r^2}$ and $d_{x^2-y^2}$ are the active orbitals if deviations from the perfect octahedral symmetry in NiO$_6$ are considered. Then, as a Hamiltonian for the Ni – O chains in the hole notation we propose

$$H = -\sum_{\langle ij \rangle, \sigma \alpha} t_{pd\sigma}(d^{\dagger}_{i\sigma\alpha}P_{j\sigma} + \text{h.c.}) + U_d \sum_{i, \alpha} n_{i\uparrow}n_{i\downarrow} + \sum_{j} n_{j} + |J_{\text{Hund}}| \sum_{i} S_{i1}S_{i2}. \quad (1)$$

$i$ ($j$) 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 $\Delta$ is the charge-transfer energy. $d_{i\sigma\alpha}$ are hole operators corresponding to a Ni site, spin $\sigma$ and orbital $\alpha$, while $p_{j\sigma}$ are oxygen hole operators. The last term in Eq.(1) is a ferromagnetic coupling between the Ni holes on different orbitals (using $S_{i\alpha} = d_{i\sigma\alpha}^{\dagger}d_{i\sigma\alpha}/2$), which enforces Hund’s rule. This term is important to produce the expected $S=1$ state in Ni$^{++}$. From an analysis of various spectroscopies for Li$_2$Ni$_{1-x}$O, it was found that $\Delta = 6.0$eV, $U_d = 9.5$eV, and $U_p = 4.6$eV. Since $U_p > \Delta$ then the compound is in the charge-transfer regime. $J_{\text{Hund}}$ is obtained from the energy levels of a (NiO$_6$)$^{10-}$ cluster. The difference in energy ($|J_{\text{Hund}}|$) between the $S=1$ $^3A$ and the $S=0$ $^1E$ levels is 1.3eV. The hopping amplitudes are $t_{pd1} = 1.3$eV and $t_{pd2} = 0.75$, according to a cluster calculation.

The study of mobile holes in model Eq.(1) is a difficult task since the energy scale is eV, while the interesting physics for $Y_{2}BaNiO_{5}$ occurs at the J-scale of about 30 meV. Thus, we need to construct an effective low-energy Hamiltonian from Eq.(1) which here we carry out following the work of Zhang and Rice in their reduction of the 2D multiband Hubbard model to the t-J model. In $Y_{2-x}Ca_xBaNiO_5$ holes populate oxygens, and they have a strong exchange $J'$ with neighboring Ni. This may lead to low energy states with $S=1/2$ or $S=3/2$, after the oxygen $S=1/2$ 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 holes 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=1/2 ground state, with the S=3/2 state located \( \sim 1.3 \text{ eV} \) higher.  

This energy difference is robust even if the parameters of Eq.(1) are modified within acceptable windows to account for experimental uncertainties. Then, proceeding à la Zhang-Rice we project out all the states of the three holes O-Ni-O cluster but the Ni-centered S=1/2 ground state.  

Eq.(1) thus reduced to an effective model with states only at the Ni sites which can be S=1 ("spins") or S=1/2 ("holes"). Thus, in our model the study of carriers on \( Y_{2-x}\text{Ca}_x\text{BaNiO}_5 \) amounts to the analysis of S=1/2 hole-like states in a S=1 background.  

To derive the allowed hole hopping processes it is important to remember the composite character of the S=1/2 hole state. To guide the intuition a graphical representation is useful (Fig.1a). The low energy states with S=1 and 1/2 located on nearest neighbors 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 with one of the Ni-holes producing a S=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=1/2 low energy state as shown in Fig.1a. 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 easily shown that the allowed processes are those listed in Fig.1b (plus their spin reversed analogs). These hopping terms have been also derived by Zaanen and Oleś using more formal arguments in their complementary presentation is useful (Fig.1a). The low energy states with S=1/2 located on nearest neighbors 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 with one of the Ni-holes producing a S=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=1/2 low energy state as shown in Fig.1a. 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 easily shown that the allowed processes are those listed in Fig.1b (plus their spin reversed analogs). These hopping terms have been also derived by Zaanen and Oleś using more formal arguments in their complementary analysis of triplet holes moving in a S=1/2 background.  

The hopping processes (Fig.1b) can be written in a compact, explicitly rotationally invariant form. The full one-band Hamiltonian then becomes  

\[
H = J \sum_{ij} \mathbf{S}_i \cdot \mathbf{S}_j - t \sum_{ij} \mathbf{P}_{ij}(\mathbf{S}_i \cdot \mathbf{S}_j + 1/2). \tag{2}
\]

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. \( J = 0.03 \text{eV} \). The second term in Eq.(2) acts only when spins 1 and 1/2 share a link. \( \mathbf{P}_{ij} \) simply permutes the two spins. The notation \( \mathbf{S}_i = (S_x, S_y, S_z) \) is used in the hopping term to indicate that this spin operator can act over both S=1 and 1/2 states depending on what spin is located at site \( i \). Their action is the standard for a spin operator. For example, \( S_1^x S_2^x |m_1^x=1, m_2^x=-1/2\rangle = \sqrt{2}|m_2^x=0, m_1^x=+1/2\rangle \). Finally, it is natural to assume that the realistic coupling regime is \( t > J \) although we have not derived \( t \) and \( J \) from Eq.(1).  

An accurate analysis of one dimensional (1D) Hamiltonians like Eq.(2) can be done using exact diagonalization (ED) techniques. \[\text{[2][21]}\] With this method, we first calculated the dispersion of one hole, \( \epsilon(q) \), using model Eq.(2) (see Fig.2a). \( \epsilon(q) \) is not symmetric with respect to \( \pi/2 \) contrary to systems with antiferromagnetic order. The minimum \( q_{\text{min}} \) at \( t/J = 2.0 \) is at \( \pi/3 \) for the chain used in Fig.2a. In the bulk limit we expect that \( q_{\text{min}} \) will move with continuity as a function of \( t/J \). While the hole ground state at most \( q \) values has \( S=1/2 \), the states close to \( q = \pi \) have \( S=3/2 \) i.e. the band in Fig.2a 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 \( 0.2 - 0.3J \) (Fig.2b) i.e. much smaller than the \( W \sim 2J \) reported for holes in 2D S=1/2 antiferromagnets. \[\text{[2]}\] 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 effective mass increases the tendency to hole localization, providing a natural explanation for the lack of true metallicity in \( Y_{2-x}\text{Ca}_x\text{BaNiO}_5 \) and in doped 2D nickelates.  

Fig.2c shows \( S(\pi, \omega) \) at a nominal hole density \( x = 1/12 \sim 0.083 \) and \( t/J = 2.0 \) calculated with ED. \[\text{[24]}\] The qualitative agreement with the INS data reported for \( Y_{2-x}\text{Ca}_x\text{BaNiO}_5 \) \[\text{[4]}\] at \( x \sim 0.04 - 0.10 \) is clear. 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=1/2 hole. To justify these identifications, let us study the q-dependence of peaks I and II (Fig.3a). Since \( S(q, \omega) \) at finite \( x \) has low-intensity structure in addition to the two main peaks (see inset of Fig.2c), the results shown in Fig.3a 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 \( \pi \), in agreement with INS \[\text{[4]}\] results where only \( q = \pi \) provided a large signal. \[\text{[23]}\]  

To better understand peak II let us study \( S(q, \omega) \) for the undoped S=1 chain with open boundary conditions (OBC) (Fig.3b). At the ends of the chain, extended S=1/2 states are formed \[\text{[24]}\] which are coupled forming singlets (S) and triplets (T), becoming degenerate as \( N \rightarrow \infty \). Peak II in Fig.3b corresponds to the transition between the S and T states. We believe this transition also contributes to \( S(\pi, \omega) \) in Fig.2c. We explicitly checked that the main contribution to peak II in Figs.2c and 3b comes from spins located near the ends of the S=1 chain. Note that on Fig.3b 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). The reason is that the "size" of the S=1/2 end-states is \( \sim 6 \) lattice spacings \[\text{[24]}\] and thus only when \( N \gg 12 \) (or the density of hole defects is \( x < 1/12 \)) is that the contribution of the S-T transition will be negligible. This lead 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 (experi-
ments thus far have only been done for $\gamma = 0.04$.

To understand the interaction between the S and T states with the hole consider first the unphysical limit $t \ll J$. In this case at low energies the dominant states are formed by the direct product of the S and T with the hole S=1/2. For a ring with N finite and even, the end-states are in a triplet state separated by a gap from the singlet combination. The triplet T couples to the S=1/2 hole forming states of S=1/2 and 3/2, denoted here as $|1/2(T)|$ and $|3/2|$, respectively. These states are split by a finite t/J, and $|1/2(T)|$ becomes the lowest energy state for a dynamical hole. The singlet S forms a S=1/2 state with the hole ($|1/2(S)|$) which is located at a higher energy. In Fig.3c results are shown for $|1/2(T)|$ and $|3/2|$ at $t/J = 0.1$. If N is odd the positions of the quasi-degenerate sextuplet $|1/2(T)| - |3/2|$, and the doublet $|1/2(S)|$ are reversed. It is remarkable that increasing t/J to realistic values the energy difference between these states remain a fraction of J. For example, in Fig.3c the energies of the $|1/2(T)|$ and $|3/2|$ states are also shown at $t/J = 2.0$. The low energy physics in S(q,ω) (at $x > 1/12$) is still dominated by the transitions between these two states. If x is reduced from $\sim 0.08$ the relative importance of these states should rapidly decrease, but for the densities used in INS ($x = 0.10$) they are very important as already shown in Fig.2c.

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=3/2 becomes the ground state at $t/J \sim 5.74$. This coupling is unrealistic and thus the high-spin states observed in the magnetic susceptibility could be caused by the presence of low energy S=3/2 Zhang-Rice holes. We also found that studying two holes on a 10 sites chain (density $x = 2/10 \sim 0.20$), the remnants of the Haldane gap are difficult to identify in S(q,ω). This prediction can be tested experimentally 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 Haldane gap states 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 $\omega$ precursors of Drude peaks should appear in severed NiO chains.

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[11] We also solved a CuO$_4$ cluster, using the three band Hubbard model parameters quoted in M. Hybertsen et al., Phys. Rev. B 39, 9028 (1989) (without $t_{pd}$ and V$_{pp}$). The energy difference between the S=0 ground state and the first S=1 state in the spectrum is $\sim 1.8 eV$ i.e. similar to the S=1/2 - S=3/2 splitting in the O-Ni-O cluster.
[12] Similar ideas were proposed by Bala et al. (Ref.12) in computing photoemission intensities for NiO.
[13] However, note that the competition between S=1/2 and S=3/2 is controversial. Adding one hole to the NiO$_6$ cluster in octahedral symmetry, van Elp et al. found a ground state with S=1/2 as in our model Eq.(1), while A. Fujimori and F. Minami, Phys. Rev. B 30, 957 (1984), reported a S=3/2 ground state. We think the ordering of the S=1/2 and 3/2 states depends on details of the parametrization of the cluster models used to fit the data. It may seem tempting to associate the states observed in the Haldane gap to transitions between these S=1/2 and 3/2 local states. However, since the natural energy scale in Eq.(1) is eV only a fine tuning of parameters produces
a 1/2-3/2 splitting of order 0.01 eV. Then, this explanation is unlikely.

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[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.2a, which complicated the analysis of $S(q, \omega)$. However, we believe the main results shown in this paper are not affected by this detail. A study of 2 holes on a 24 site chain is not possible numerically.

[23] While peak II in Fig.2c 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.

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Figure Captions

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 1/2 spin states of Eq.(2) at two arbitrary sites i and j, respectively. $P_{i\rightarrow j}$ in Eq.(2) enforces the absence of the hopping $|1, -1/2 \rightarrow 1/2, 1 \rangle$. The spin projections only change by 1/2 or -1/2 at each site.

2. (a) $\epsilon(q)$ on a $N = 12$ 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.

3. (a) Energy of the excitation with the highest intensity in $S(q, \omega)$ (parameters as in Fig.2c). 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 (defined in the text) $|1/2(T)\rangle$ and $|3/2\rangle$, respectively, at $t/J = 0.2$. Full squares and circles correspond to $|1/2(T)\rangle$ and $|3/2\rangle$, respectively, at $t/J = 2.0$. 

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