Spin dynamics of hole doped Y$_2$BaNiO$_5$

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Starting from a multiband Hamiltonian containing the relevant Ni and O orbitals, we derive an effective Hamiltonian $H_{eff}$ for the low energy physics of doped Y$_2$BaNiO$_5$. For hole doping, $H_{eff}$ describes $O$ fermions interacting with $S=1$ Ni spins in a chain, and cannot be further reduced to a simple one-band model. Using numerical techniques, we obtain a dynamical spin structure factor with weight inside the Haldane gap. The nature of these low-energy excitations is identified and the emerging physical picture is consistent with most of the experimental information in Y$_{2-x}$Ca$_x$BaNiO$_5$.

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The properties of antiferromagnetic (AFM) chains have been a major topic in the study of low dimensional magnetism. Haldane's conjecture about the existence of a gap in spin $S=1$ one dimensional (1D) Heisenberg systems has inspired a considerable amount of research. Recently, there has been wide interest in Y$_2$BaNiO$_5$, a near ideal realization of the S=1 AFM Heisenberg chain, and the effects of different dopants on specific heat, and magnetic properties. While replacement of Ni$^{2+}$ ($S=1$) by non-magnetic Zn$^{2+}$ or Mg$^{2+}$ simply cuts the spin chains, the replacement of off-chain Y$^{3+}$ by Ca$^{2+}$ introduces holes primarily on oxygen sites. In the last case, resistivity decreases by several orders of magnitude, and inelastic neutron scattering reveals new states inside the Haldane gap. In addition, the magnetic behavior of the Ca doped system, markedly different from the Mg-doped one, is spin-glass like with a characteristic temperature $T_g \sim 2K$.

It has been shown that spin models with localized site or bond impurities lead to in-gap states for certain parameters. While the results are interesting, these models can only be valid for completely localized added holes, which seems not to be the case in Y$_{2-x}$Ca$_x$BaNiO$_5$. Models for mobile holes have been studied, but with effective hole hopping $t$ more than one order of magnitude smaller than realistic values.

In Ref. we find no bound states in this static case. Thus, the origin of the observed states inside the Haldane gap in Y$_{2-x}$Ca$_x$BaNiO$_5$ is not yet clear.

In this Letter, we start from a multiband Hamiltonian $H_{mb}$ for NiO$_5$ linear systems, containing all essential orbitals and interactions. An effective low-energy Hamiltonian $H_{eff}$ is derived. By exact diagonalization of $H_{eff}$, we provide an explanation of the observed inelastic neutron spectrum. In addition, our results are consistent with the measured gap, x-ray absorption spectrum, magnitude of the intra- and inter-chain exchange, magnetic susceptibility and muon spin relaxation.

The starting Hamiltonian is the extension to the 1D NiO$_5$ system of the one used by van Elp et al. for a NiO$_6$ cluster, restricting the basis of Ni orbitals to the $3d_{3z^2-r^2}$ and $3d_{2z^2-y^2}$ ( $z$ is the direction along the chain):

$$H_{mb} = \sum_{i\alpha} c_i^\dagger c_i + \sum_{i\neq j} t_{ij} \alpha^\dagger \beta_i \phi_{j\alpha} \phi_{j\beta} + \sum_{i\alpha} (U_i + J^H_i) n_{i\alpha} \phi_{i\alpha} + \sum_{iJ} J^H_i (\phi_{i\alpha}^\dagger \phi_{i\beta})^2/2 - S_{i\alpha} \cdot S_{i\beta} + \sum_{i\neq j} U_{ij} n_{i\alpha} m_{ij\beta}$$  \hspace{1cm} (1)

where $c_{i\alpha}$ creates a hole with spin $\sigma$ on the orbital $\alpha$ of site $i$. The interactions included are the on-site Ni repulsion $U_d$, Ni Hund interaction $J^H$ (for O sites $J^H_i = 0$, O on-site repulsion $U_p$ and Ni-O NN repulsion $U_{pd}$, for the six O atoms surrounding a Ni one. For simplicity, the basis of O orbitals considered is reduced to the $2p_z$, and the two linear combinations of $2p$ orbitals lying in the $xy$ plane having optimum hybridization with their NN Ni orbitals (the amount of other $2p$ states, in the low energy manifold, is of the order of 1%). From atomic data we obtain $J^H = 1.6eV$. From Ref. $U_d = U(3E_g) = 10eV$. The values of $U_p = 4eV$ and $U_{pd} = 1.2eV$ were taken from Ref. The hopping parameters were taken from...
model for the cuprates. The toemission and magnetic properties of the three-band cal transformation. For hole doping also calculated the exchange along \( b \) perpendicular one. Taking into account that \( \Delta \) should increase to the left of the periodic table, and \( \Delta = \epsilon_p - \epsilon_d + U_{pd} \sim 4.8 \text{eV} \) in the cuprates. To gain further confidence on the resulting parameters, we have compared other two quantities with experiment. Solving exactly \( H_{mb} \), including the repulsion \( V_d \) (\( V_p \)) between a Ni 2p\(_3/2\) core hole and a Ni 3d (NN O 2p) hole in a NiO\(_6\) cluster, we have calculated the shift towards lower energy in the Ni L\(_3\) x-ray absorption spectrum in going from polarization along the chain to a perpendicular one. Taking \( V_d - V_p = 10 \text{eV} \) we obtain 0.80eV, while the experimental shift is 0.91eV. We have also calculated the exchange along \( b \) direction (perpendicular to the chains) \( J_b \), starting from the exact solution of two NiO\(_6\) clusters, and treating the hoppings connecting the two clusters with the cell-perturbation method. We obtain \( J_b = 0.173K = 6.4 \times 10^{-4}J \), near the upper bound \( 5 \times 10^{-4}J \) estimated in Ref. \[4\].

The low-energy reduction procedure \[4\] which we found most convenient for the present problem is the one used successfully in Ref. \[2\] to reproduce low-energy photoemission and magnetic properties of the three-band model for the cuprates. The form of the low-energy effective Hamiltonian \( H_{eff} \) is determined by a canonical transformation. For hole doping \( H_{eff} \) has the form of a spin-fermion \( H_{sf} \)(or Kondo-Heisenberg) model as in Ref. \[4\]. For electron doping, \( H_{eff} \) has the form of a one-band model \( H_{ib} \) (Eq. (3) with \( J' = 0 \) and \( t = -0.351 \text{eV} \)). The procedure eliminates linear terms in the Ni-O hopping, retaining second order contributions and the fourth-order exchange \( J \). However, the values of the parameters are determined fitting the energy levels of \( H_{eff} \) to the corresponding ones of \( H_{mb} \) in conveniently chosen clusters (Ni\(_2\)O\(_4\) for electron-doped and NiO\(_6\) for hole-doped systems). \( H_{sf} \) can be written as:

\[
H_{sf} = \sum_{i\delta\sigma} p_{i+\delta\sigma}^\dagger p_{i-\delta\sigma} \left[(t_1 + t_2) \left(S_i \cdot \Sigma_{i-\delta} + \frac{1}{2}\right) - t_2\right] + J_K \sum_{i\delta} \left(S_i \cdot \Sigma_{i+\delta} - \frac{1}{2}\right) + J \sum_{i\delta\sigma} S_i \cdot S_{i+2\delta} + \frac{\epsilon}{2} \sum_{i\delta\sigma} p_{i+\delta\sigma}^\dagger p_{i+\delta\sigma}
\]

(2)

Here \( i \) labels a Ni site, and \( i + \delta \) denotes its two NN O atoms along the chain, \( p_{i+\delta\sigma}^\dagger \) creates an effective 2p\(_2\) hole (it contains information of other Ni and O orbitals) of spin \( \sigma \) at site \( i + \delta \), and \( S_i \) (\( \Sigma_{i+\delta} \)) is an effective spin \( 1 \) (\( 1/2 \)) at site \( i \) (\( i + \delta \)). We obtain \( t_1 = 0.64 \text{eV}, t_2 = 0.89 \text{eV} \) and \( J_K = 1.40 \text{eV}; \epsilon = 8.97 \text{eV} \) is irrelevant for the spin dynamics, but determines the charge gap \[3\].

In Fig.1(a) we show the dynamical structure factor \( S(\omega, \pi) \) of O(NiO\(_2\))\(_{10}\) system with open boundary conditions and one (zero) added hole. (b) Correlation functions \( E(\omega), M(\omega) \) and \( L(\omega) \) defined in the text.

![FIG. 1. (a) Full (dashed line: dynamic structure factor \( S(\omega, \pi)/5 \) of O(NiO\(_2\))\(_{10}\) system with open boundary conditions and one (zero) added hole. (b) Correlation functions \( E(\omega), M(\omega) \) and \( L(\omega) \) defined in the text.](image-url)
thermodynamic limit, since Ca doping does not break the chains. This suspicion is confirmed by inspection of the correlation function $E(\omega) = \int dt \ e^{i\omega t} \ \langle \frac{1}{2} \ | O(t)O(0) | \frac{1}{2} \rangle$ where $O = \sum_j e^{-j(1+\pi)}S_j^z$ and $|m\rangle$ is the component with $S^z = m$ of the $S=3/2$ ground state. $E(\omega)$ measures the response of the system to an excitation localized at one end of the chain. The result is shown in Fig.1(b).

There is an intense structure around 3meV consisting of three peaks. The first and the third one are practically identical, while the second one is much less intense. This second peak, which is located at 0.6meV for O(NiO$_2$)$_8$, tends to vanish with increasing doping. This effect can be interpreted in terms of a NN attractive interaction between the latter spin and the one inside the polaron, rendering cumbersome to obtain $H_{1b}$ as an expansion in powers of the overlap $P_1$. We then construct orthogonal Wannier functions $\eta_i$ at each Ni site, write $H_{sf}$ in this basis using $p_i = (2/\pi) \sum_n (-1)^{n+1}(2n-1)^{-1} \pi_{i+n,\sigma}$, calculate $P_iH_{sf}P_1$ ($P_1$ is a projector over local orthogonal Zhang-Rice doublets), and map it into $H_{1b}$. Unfortunately, contrary to the case of the cuprates, $P_1$ does not commute even approximately with $H_{sf}$ in any limit. Local quadruplets are important in the low energy physics. Assuming for simplicity $J_K = t_1 + t_2$, and including only the two largest terms (besides $J$) we obtain:

$$H_{1b} = \sum_{j\delta} \left[ t \ P_{j,j+2\delta} (\tilde{S}_j \cdot \tilde{S}_{j+2\delta} + \frac{1}{2}) - J' \tilde{S}_j \cdot \tilde{S}_{j+2\delta} \right] + J \sum_i \tilde{S}_i \cdot \tilde{S}_{i+1}$$

Here $j$ runs over the positions of the Zhang-Rice $S=1/2$ spins $\tilde{S}_j$ and $P_{j,j+2\delta}$ permutes $\tilde{S}_j$ with its nearest $S=1$ spins $\tilde{S}_{j+2\delta}$. The resulting values of $t$ and $J'$ are $t = 0.36t_1 + 1.027t_2 \sim 1eV \sim 40J$, and $J' = 0.181J_K \sim 0.25eV$, in agreement with simple expectations. The $S(\pi,\omega)$ obtained using $H_{1b}$ is very different from that of $H_{sf}$ and displays only one peak (around 6meV) below the Haldane gap. This result is in fact more similar to the response of the undoped system.

![FIG. 2. (a) Top: schematic representation of the ground state of $H_{sf}$ for one added O hole (indicated by the small up arrow). The dashed line indicates a region in which the interchain interactions $J_{ij}$ are frustrated due to the change of the interchain short-range magnetic correlations produced by the O hole. (b) The same for the first excited state. The Ni states with $S^z = 1,0,-1$ are indicated by ↑, 0, ↓ respectively.](image-url)
To shed light onto the underlying physics, it is instructive to solve $H_{af}$ in a Ni$_3$O$_2$ chain. The ground state has $S=5/2$ and is nearly degenerate to an $S=3/2$ state. Except for the parity of the wave functions, the result can be interpreted as if the central static ZRDs were strongly FM coupled to one of the neighboring Ni spins and very weakly FM coupled to the other one. This quasidegeneracy is not obtained with $H_{1b}$ for any set of parameters, indicating that the inclusion of quadruplets is crucial to have this weak link. This image is confirmed by the analysis of the dominant terms in the wave function of the ground and first excited states represented in Fig. 2, and provides a plausible explanation of the susceptibility measurements of Kojima et al. at temperatures above the effective exchange of the weak link, the chains behave as being cut, and a segment between two ZRDs can have zero, one or both ZRD’s FM coupled with it, with probabilities 1/4, 1/2 and 1/4 respectively. If the number of Ni atoms in the segment is even, the spin of the segment is zero. Then, the corresponding total spin of the segment plus coupled ZRD’s is 0, 1/2, 0 for the three cases respectively. If the number of sites in the segment is odd, the spin of the segment is equal to 1 and the corresponding total spin is 1, 3/2 and 2 respectively. This gives an average $\langle S(S + 1) \rangle = 17/8$ in excellent agreement with the observed Curie constant.

An important feature of the ground (first excited) state of $H_{af}$ in the 10-site chain, is that the end spins display FM (AFM) correlations. When the interchain exchange $J_0$ is included, this implies that for 10% Ca doping, near five Ni spins have the wrong sign of the magnetic correlations with neighboring chains, implying a frustration energy of roughly 20$J_0$ = 3.2K (see Fig. 2). Since this energy is within the order of magnitude of the randomness (due to disorder) distributed lowest excitation energies, a spin glass behavior with characteristic temperatures near 3K is expected, in agreement with experiment.

In summary, starting from a multiband Hamiltonian similar to a one used previously for NiO but including only 3d $e_g$ orbitals, we have derived a low-energy Hamiltonian for doped Y$_2$BaNiO$_5$, and used it to understand magnetic properties of the Ca doped system, particularly the additional states include the Haldane gap. Contrary to previous predictions we obtain that these states are quite different to these produced by Zn doping and substantial weight near the middle of the Haldane gap is obtained only for Ca doping.

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