Specific heat of defects in the Haldane system Y_2BaNiO_5

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We calculate the specific heat $C(B,T)$ of the antiferromagnetic spin-1 chain compound $Y_2BaNi_{1-x}Zn_xO_5$ as a function of magnetic field B and temperature T. The low-energy spectrum of an anisotropic Heisenberg Hamiltonian has been solved using the density-matrix renormalization-group theory. Considering the experimental values for the parameters and an approximate model for interchain interactions the observed $C(B,T)$ is quantitatively reproduced. For large chains ($N>50$) we find asymptotically free $S=1/2$ states. Our results are thus also consistent with electron-spin-resonance data for NENP. [S0163-1829(98)05137-6]

A great deal of interest in one-dimensional (1D) Heisenberg chains with nearest-neighbor antiferromagnetic (AF) exchange coupling J, has been originated by Haldane's conjecture that integer-valued spin chains would exhibit a gap in the spin-wave excitation spectrum,[1] in contrast to half-integer spins which would be gapless.[2] This quantum many-body phenomena is different from the usual source of gaps in magnets, namely, single-ion anisotropy, which does not involve correlation effects. Subsequent observations of large gaps in spin-1 quasi-one-dimensional systems have confirmed Haldane's observation. Affleck *et al.*[3] have shown that the exact ground state of the Hamiltonian $\Sigma_i \mathbf{S}_i\mathbf{S}_{i+1} + (\mathbf{S}_i\mathbf{S}_{i+1})^2/3$ is a valence-bond-solid (VBS) state. In this state, each $S=1$ spin is represented by symmetrization of two $S=1/2$ entities. These $S=1/2$ spins at each site are coupled with nearest-neighbor $S=1/2$ spins, one to the left and the other to the right, to form singlets. Hence, an open chain has two unpaired $S=1/2$ spins, one at each end. In agreement with this model, exact diagonalization[4] of finite open chains shows that the four lowest-lying states are a triplet and singlet whose energy separation approaches zero exponentially with increasing length. Monte Carlo[5] and density-matrix renormalization-group[6] (DMRG) studies clearly show the presence of $S=1/2$ end states. This picture is also supported by electron-paramagnetic-resonance (EPR) measurements of NENP doped with nonmagnetic ions,[7] where resonances corresponding to the fractional spin $S=1/2$ states at the ''open'' ends of the Ni chains were observed. Similar measurements for doping with magnetic ions are also consistent with $S=1/2$ end states.[8]

However, Ramirez *et al.*[9] also tested the presence of free $S=1/2$ states by studying the specific heat of defects in NENP and Y_2BaNiO_5, with magnetic fields up to 9 T and temperatures down to 0.2 K. On the basis of a comparison between two very simplified pictures, they found that the shape and magnitude of the Schottky anomaly associated with the defects in $Y_2BaNi_{1-x}Zn_xO_5$ are well described by a simple model involving spin-1 excitations, instead of the $S=1/2$ excitations of the VBS. These results are in contrast with the above-mentioned EPR measurements of NENP.[7] While previous theoretical studies of the spin-1 Heisenberg chain[4–6] confirm the existence of free $S=1/2$ spins at the ends of sufficiently long chains in agreement with the EPR measurements, it seems difficult to reconcile these results with the specific-heat measurements and no theoretical calculation of the latter exists so far.

In this paper, we solve the low-energy spectrum of the appropriate Hamiltonian which describes the Ni chains of Y_2BaNiO_5 using DMRG and finite-size scaling. Assuming that defects are randomly distributed, we can calculate the specific heat for any concentration of nonmagnetic impurities. Our results show that there is no contradiction between EPR[7] and specific-heat measurements in $Y_2BaNi_{1-x}Zn_xO_5$.[9] They confirm the existence of spin-$\frac{1}{2}$ excitations for sufficiently long chains and are in good agreement with the curves measured by Ramirez *et al.*[9] To obtain a precise fit of all data, particularly those for $B=0$ and high doping, we include interchain exchange.

Y_2BaNiO_5 has an orthorhombic crystal structure with the Ni^{2+} ($S=1$) ions arranged in linear chains with a nearest-neighbor AF superexchange coupling J. The interchain coupling $J_\perp$ is three orders of magnitude weaker, making this compound an ideal one-dimensional antiferromagnetic chain. While the Ni is surrounded by six O atoms in near octahedron coordination, the true site symmetry is D_{2h}. Neglecting $J_\perp$ for the moment, the appropriate Hamiltonian for a chain segment of length N between two Zn impurities is[10–12]

$$H=\sum_i \{J\mathbf{S}_i\mathbf{S}_{i+1}+D(S_i^z)^2+E[(S_i^x)^2-(S_i^y)^2]\}-g\mu_B\mathbf{B}\mathbf{S}_t,$$

where z is along the chain axis and $\mathbf{S}_t$ is the total spin. Recent estimates based on fits of the Haldane gaps (in x, y, and z directions) measured by inelastic neutron scattering, indicate $J\sim 280$ K, $D\sim -0.039J$, and $E\sim -0.014J$.[10,11] As Y_2BaNiO_5 has a Haldane gap ~ 100 K,[10,11] the spin-wave contribution to the specific heat is negligible below 7 K. In this temperature range, $C(B,T)$ is dominated by the effect of the defects, which is manifested as a $1/T^2$ rise in $C(B,T)/T$, and a Schottky anomaly in the presence of an applied magnetic field. The height and width of the Schottky anomaly strongly depends on the spin value of the low-energy excitations. For these reasons, it is necessary to solve the low-energy spectra ($\omega \leqslant 10$ K) of H for all values of N to have an accurate theoretical picture.

By means of the DMRG method, we have calculated the two lower eigenenergies in the $S_t^z=0$ subspace and the lower one with $S_t^z=1$ (this state is degenerated with the $S_t^z=-1$ due to the time-reversal symmetry of H) for all $N\leqslant 40$ and $E=0$. The energy difference between the excited states and

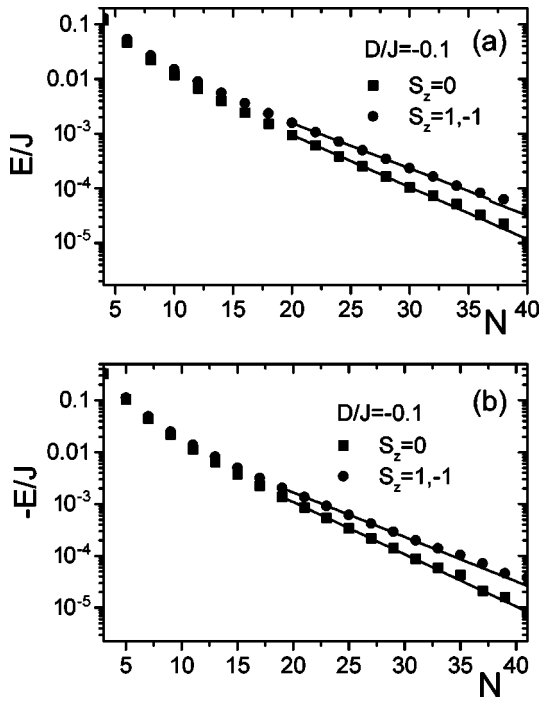

FIG. 1. Difference between the energy of the *triplet* $S_z = \pm 1$ ($S_z = 0$) and the singlet states in the presence of anisotropy D are denoted with circles (squares) . (a) N even, (b) N odd. The full line is an exponential fit of these differences for $N \geqslant 19$.

the ground state decays exponentially to zero with increasing N. This behavior, shown in Fig. 1 for an arbitrary value of anisotropy $D=-0.1$, allows us to extrapolate the energies to all values of $N>40$, and demonstrate that the free $S=1/2$ spins at the end of the chain persist in presence of anisotropy. This issue is easy to understand considering that $S=1/2$ spins cannot be affected by anisotropy due to time-reversal symmetry. At this level, it is important to remark that the two $S=1/2$ spin excitations, predicted by VBS, have a finite localization length $l \sim 6$ sites.[4–6] Therefore, while they are nearly free for large ($N>>l$) open chains, the interaction between them is considerable when the length of the chain N is comparable to $2l$. This interaction splits the two $S=1/2$ states into a singlet (ground state for even N) and a triplet (ground state for odd N) one.[13]

The difference between any two energies of the above mentioned low-energy states is linear in D, and the quadratic corrections are negligible.[12] This widely justifies the validity of perturbation theory to first order in D. Then, by symmetry we can include the term $\Sigma_i E[(S_i^x)^2-(S_i^y)^2]$ to first order. Thus we find the following low-energy effective Hamiltonian including a spin $S=1$ and a singlet state $|0\rangle$:

$$H_{eff}=E_0(N)+\alpha(N)|0\rangle\langle 0|+D\beta(N) \times S_z^2+E\beta(N)(S_x^2-S_y^2)-g\mu_B \mathbf{BS},$$

where $E_0(N)$, $\alpha(N)$, and $\beta(N)$ are functions of the chain length N (determined from the DMRG data). The validity of the last term has been verified explicitly by calculating the matrix elements of S_t^+, and S_t^- for all chains. Neglecting $J_\perp$, $H_{\rm eff}$ determines the thermodynamics of the system at temperatures well below the Haldane gap.

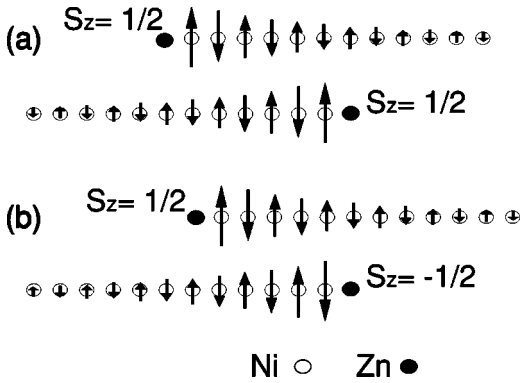

FIG. 2. Scheme of the configuration of minimum interchain interaction energy involving two $S=1/2$ end states. (a) and (b) correspond to an effective ferro- ($n=7$, see text) and antiferromagnetic ($n=6$) interaction, respectively.

For a random distribution of defects, the specific heat per elementary cell of Zn-doped Y_2BaNiO_5 is

$$C(B,T)=\sum_{N=1}^{\infty} x^2(1-x)^N C_N(B,T),$$

where $C_N(B,T)$ is the specific heat of a segment of length N described by $H_{\rm eff}$, and x is the concentration of missing Ni atoms. As we shall see, this equation describes qualitatively well the experiments. However, it neglects interactions between chain segments. Among then the largest one is the Ni-Ni interchain exchange interaction along the y direction $J_\perp$, which can be estimated by sixth order perturbation theory in the relevant hoppings. Similarly, using eigth-order perturbation theory we estimate the order of magnitude of the interaction across a Zn impurity $J_{\rm Zn}$ to be less than 0.1 K. Although the exact value is very sensitive to the values of the hoppings, J_{Zn} is, in any case, below the lowest temperature accessible in the specific-heat measurements (0.2 K).[9] To obtain an accurate estimate of $J_\perp$ we solved exactly two NiO_6 clusters including all relevant orbitals and interactions and calculated $J_\perp$ by second-order perturbation theory in the intercluster hoppings.[14] Using the values of the hoppings taken from NiO (Ref. 15) scaled appropriately with distance,[14] we obtain $J_\perp = 0.88$ K. However, due to uncertainties in the hopping parameters, $J_\perp$ could be as low as 0.17 K.[14] The expectation value of the spin at each site $\langle S_i^\eta \rangle$ along the direction η of maximum projection of the $S=1/2$ spin of an end state has an alternating zig-zag structure extending $l \sim 6$ lattice sites[5,6] (see Fig. 2). Thus, to lowest order in $J_\perp$, the magnitude of the effective interaction J' between end states lying in nearest chains in the y direction can vary from a few K, if the difference n between the z coordinates of the Zn defects is small, to zero if $n \geqslant 6$. The sign of J' is that of $(-1)^n$ (Fig. 2).

Since a calculation of all possible J's and their effect on a 2D (or 3D) topology is a formidable task, we model the effect of J' considering a collection of chain segments with effective 1D topology with exchange interaction J' between two consecutive segments, with a random and uniform distribution between $-J'_{\rm max}$ and $J'_{\rm max}$. Each segment is described by $H_{\rm eff}$. The specific heat is calculated from the exact solution of this model in systems of up to eight sites

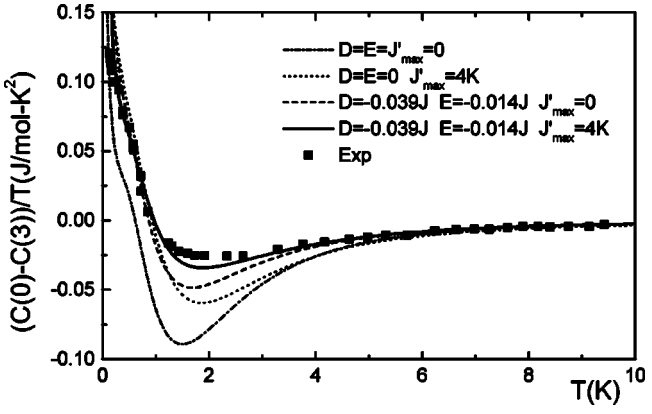

FIG. 3. Specific-heat difference between 0 and 3 T for $Y_2BaNi_{0.96}Zn_{0.04}O_5$ for several parameters.

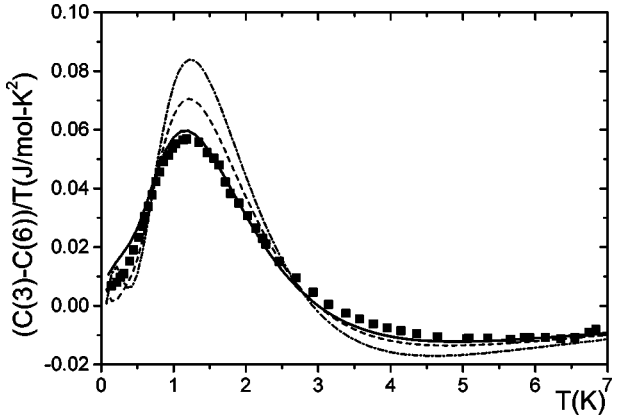

FIG. 4. Specific-heat difference between 3 and 6 T for $Y_2BaNi_{0.96}Zn_{0.04}O_5$. Symbols are the same as in Fig. 3.

(finite-size effects are negligible), averaging over 500 different realizations of segment lengths and values of J' with the given probability distributions, and integrating over all possible directions of B. We have taken the above-mentioned experimental values for J, D, and E.[10,11] An anisotropic g value ($g_z=2.25$, $g_x=g_y=1.17$) was taken from Ref. 16. The only fitting parameter is $J'_{\max}$, which is however bounded by the above estimate.

In Fig. 3 we represent the experimental data for $[C(0,T)-C(3\mathrm{T},T)]/T$ with $x=0.04$, scanned from Ref. 9, and compare it with different theories. The difference between two different values of B, eliminates the contribution of phonons, two-level systems, or any field-independent contribution to $C(B,T)$. The Heisenberg model without anisotropy and interchain interactions, is unable to reproduce the $B=0$ data. The singlet-triplet model proposed in Ref. 9, is even worse, because it leads to $C(0,T)=0$ for $T>0$. Including realistic anisotropy, there is already a considerable improvement, and the remaining discrepancy is removed by our treatment of the interchain interactions with $J'_{\max}=4$ K. This value is consistent with our estimate of J' explained above, and of the order of the spin-glass temperature observed in the Ca-doped system,[17] for which frustration effects due to $J_\perp$ are expected.[14] It is clear from Fig. 3 that the main correction to the result of the ideal isotropic 1D Heisenberg chain, is due to anisotropy which is treated with high accuracy.

As expected, when $g\mu_B B \gtrsim J'$ the effect of $J_\perp$ decreases for larger B. In Fig. 4 we compare experiment and theory for $[C(3\mathrm{T},T)-C(6\mathrm{T},T)]/T$ for $x=0.04$. Considering anisotropy alone explains qualitatively the experiment. This is also true for Fig. 4 in Ref. 9 corresponding to nominally undoped Y_2BaNiO_5, which can be reasonably well fitted with $J'_{\max}=0$ with $x=0.28$. Note that as x is lowered, the distribution of different J' should be displaced towards $J'=0$, and for sufficiently low x (when the average length of the chains is much larger than l), the effect of J' should be negligible. In contrast, if a sizeable J_{Zn} were present, its effect would persist for low x.

From Figs. 3 and 4 it is clear that the inclusion of interactions between end $S=1/2$ spins through the chain via the full Hamiltonian H, together with anisotropy, eliminates the apparent discrepancy between VBS theory predictions and measured specific heat.[9] In Fig. 5 we have separated the contributions of different chain lengths to $[C(3\mathrm{T},T)-C(6\mathrm{T},T)]/T$, neglecting J'. The full line corresponds to the result for noninteracting $S=1/2$ end spins. This behavior is obtained for $N\gtrsim 50$ where the singlet-triplet gap is much smaller than $g\mu_B B$. The effect of anisotropy is stronger for shorter chains, changing the position and height of the Schottky peak. This behavior is mainly due to odd chains because they have an $S=1$ ground state. The anisotropy splits the $S_z=0$ and $S_z=\pm 1$ (ground state for $D<0$) triplet states, and the energy separation $\Delta(N)$ decreases with N (as can be inferred from Fig. 1). As one can see from Fig. 5, for large chains, the result approaches asymptotically the VBS prediction, i.e., the peak is higher and shifted to slightly smaller temperatures. However, the curves for shorter chains ($\Delta(N)\gtrsim g\mu_B B$) show the opposite behavior, and both tendencies are compensated in the final result. To understand this effect let us consider the simplest case of $E=B_x=B_y=0$ and odd N. The energy difference corresponding to the Schottky anomaly, $E(S_z=0)-E(S_z=-1)$, becomes $g\mu_B B_z+\Delta(N)$ when a magnetic field is applied. This explains the shift to the right registered for the shorter chains. As a consequence, the sum over small ($N\lesssim 20$) values of N, weighted with the Poisson distribution, yields a Schottky peak of larger width and lower height. The anomalous fea-

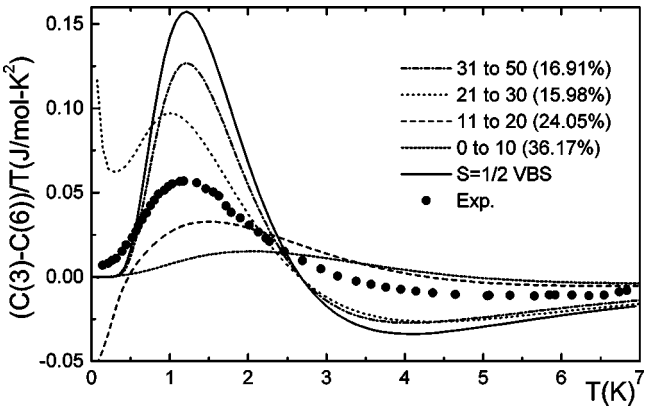

FIG. 5. Contributions of chains in different length intervals to the specific-heat difference between 3 and 6 T neglecting interchain interactions. The full line corresponds to the prediction of VBS theory for noninteracting $S=1/2$ moments. The final result (Fig. 4) is obtained adding each curve with the weight denoted inside the figure.

tures at low temperature in Figs. 4 and 5 are due to the contributions of chains with even N for which the difference between the energy of the triplets with $S_z=\pm 1$ and the singlet ground state becomes of the order of the Zeeman energy $g\mu_B B$. For 6 T this crossing occurs for N between 18 and 20 giving rise to the large negative contribution for the corresponding curve in Fig. 5. For $B=3$ T the crossing occurs for N between 22 and 24 (see the $21\leqslant N\leqslant 30$ curve in the same figure).

Our results allow us to understand why the $S=1$ states of short chains were not seen in the EPR experiments in NENP.[7] For $D/J\sim 0.2$ the splitting $\Delta(N)$ is greater or of the order of the applied magnetic field $g\mu_B B_a$ ($B_a\sim 0.35$ T) when $N<38$, while for $N>54$, $\Delta(N)<0.1 g\mu_B B_a$. Among these larger chains (76% of the total number of chains for $x=0.005$), a fraction of the order of 90% is not affected by J' and contribute to the same EPR signal with total weight 0.0038 per transition-metal atom. On the other hand, each of the chains with $N<38$ (weight $\lesssim 0.0002$), resonates at different gyromagnetic frequency, larger than the one they considered.[7]

In conclusion, by solving the low-energy spectrum of a Heisenberg Hamiltonian H which includes experimental axial and planar anisotropy, and (approximately) the effect of interchain exchange through the only fitting parameter $J'_{\max}$, we have reproduced the low-temperature specific-heat data measured in $Y_2BaNi_{1-x}Zn_xO_5$ for different magnetic fields.[9] Our results are consistent with valence-bond-solid predictions of $S=1/2$ chain end excitations, which are asymptotically free for large chain segments. However, the intrachain interactions for short segments are critical for the understanding of the specific-heat behavior. These results remove the apparent discrepancy between the specific-heat data for Y_2BaNiO_5, interpreted in Ref. 9 with a singlet-triplet model, and electron paramagnetic resonance data for NENP.

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