On-site magnetization in open antiferromagnetic chains: A classical analysis versus NMR experiments in a spin-1 compound

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The response of an open spin chain with isotropic antiferromagnetic interactions to a *uniform* magnetic field is studied by classical Monte Carlo simulations. It is observed how the induced on-site magnetization is *nonuniform*, due to the occurrence of edge staggered terms which decay exponentially over a distance equal to the zero-field correlation length of the infinite chain. The total magnetic moment associated to each staggered term is found to be about half of the original single-spin magnitude and to decrease as the inverse of temperature (i.e., to behave as a Curie-like moment). The numerical results are compared to recent NMR findings in spinless-doped Y_2BaNiO_5; the remarkable agreement found shows that, for temperatures above the Haldane gap, the classical approach gives a correct picture of the boundary effects observed in the Heisenberg $S=1$ chain.

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Because of the richness of their phase diagrams, Heisenberg spin systems with low-dimensional antiferromagnetic interactions (HAF's) are presently attracting strong interest. Magnetic correlations in spatially homogeneous HAF's have been probed dynamically, in Fourier space, by neutron scattering, but can hardly be visualized experimentally in a static real-space picture. Translational invariance, in fact, makes each site equivalent to the others, thus preventing any spatial oscillation of the spin direction. In recent experiments, the correlation properties of low-dimensional HAF's have been investigated through NMR imaging of the spin polarization induced by a uniform field around nonmagnetic defects that break the translational invariance. Relevant results have been obtained in copper oxide two-dimensional compounds,[1,2] in spin ladders,[3] and in half-integer[4] and integer spin chains.[5]

In $S=1$ chains in particular, the local magnetization $\langle S_i^z \rangle$ has been resolved *site by site*, through ^{89}Y NMR in Mg-doped Y_2BaNiO_5,[5] for temperatures ranging from $T \simeq 0.35J/k_B$ to $T \simeq J/k_B$, being J the AF exchange constant. $\langle S_i^z \rangle$ shows an alternate component which is maximum around impurities (i.e., close to chain boundaries) and vanishes exponentially over a distance equal to the zero-field correlation length of the bulk. Boundary staggered defects with total spin $S=1/2$ and a size of the order of the bulk correlation length are actually expected, for $S=1$ HAF chains, in the limit $T \to 0$. At very low temperatures in fact, the magnetic properties of these systems are controlled by edge-induced triplet states,[6,7] in which $\langle S_i^z \rangle$ shows the profile described above.[8–11] This $T \simeq 0$ argument, however, can hardly be used by itself in order to explain the experimental evidences in Ref. 5, since—on increasing temperature - the excited states above the Haldane gap $\Delta_H \simeq 0.4J$ should be taken into account (in open $S=1$ chains Δ_H corresponds to the separation between the second and the third lowest-lying energy levels[6]). A finite-temperature analysis, in which all the excited states are correctly treated, was recently carried out by Alet and Sørensen,[12] using quantum Monte Carlo techniques. Excellent agreement with the experimental data derived from NMR imaging[5] has been obtained.

The purpose of the present work is to study whether or not the alternating magnetization observed in finite $S=1$ chains is a pure quantum-mechanical effect somewhat reminiscent of the liquidlike ground state. The response of open chains with various lengths L to a uniform magnetic field is thus studied in the limit of infinite S, proving that *edge staggered defects with spin-S/2 originate from the translational invariance breaking, even in the framework of a classical model*. It is shown that the characteristic spatial extention of these defects corresponds to the zero-field correlation length of the thermodynamic chain ($L \to \infty$) and that, at high temperature, the behavior of $\langle S_i^z \rangle$ calculated for infinite S tracks the experimental findings in the $S=1$ chain.

In the classical limit ($S \to \infty$), the Hamiltonian for a nearest-neighbor Heisenberg chain of L sites in an external field H takes the form

$$\mathcal{H} = J \sum_{i=1}^{L} \vec{S}_i \cdot \vec{S}_{i+1} - g\mu_B H \sum_{i=1}^{L} S_i^z, \qquad (1)$$

where $\vec{S}_i$'s are classical vectors, whose magnitude is taken to be $|\vec{S}_i| = \sqrt{S(S+1)}$ (i.e., $|\vec{S}_i| = \sqrt{2}$ in this case), and J is positive for antiferromagnets.

The thermal expectation value of the on-site magnetic moment has been calculated by the Wolff[13] cluster algorithm in the temperature range $50 \leqslant T \leqslant 285$ K, for L up to 31 spins. In order to compare numerical data with NMR results in doped Y_2BaNiO_5, J/k_B has been set equal to 285 K.[14] The effect of the magnetic field H has been included using a standard Metropolis algorithms, which associates a flip probability to the whole cluster. As the field intensity is low, the flip acceptance remains close to 1.

Typical results of the simulations for different values of H are shown in Fig. 1, proving that the response of a finite classical chain to a homogeneous field is nonuniform. In Fig. 2, magnetization profiles at characteristic temperatures and $H=14.1$ T, are shown together with ^{89}Y NMR spectra in Mg-doped Y_2BaNiO_5 (at the same temperatures) from Ref.

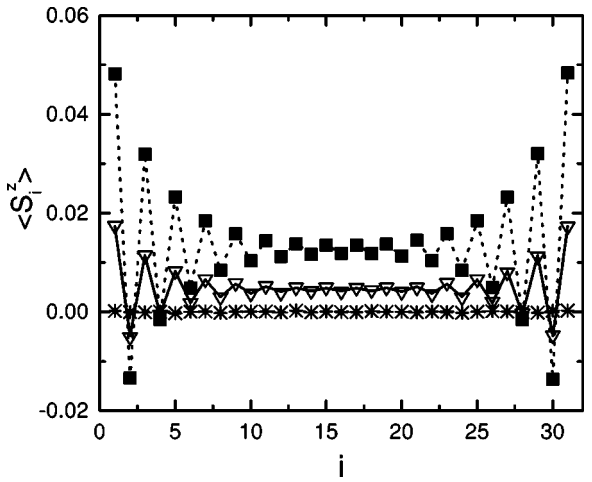

FIG. 1. Magnetization profiles at $T=150$ K, obtained by classical Monte Carlo in a $S=1$ chain of 31 sites with $J/k_B=285$ K. Different symbols correspond to different applied fields: $H=0$ (stars), $H=5$ (triangles) and $H=14.1$ T (squares).

5. The spectra were obtained at fixed frequency ($\nu_{rf}=29.4$ MHz) by sweeping the magnetic field H_0 in a narrow range around 14.1 T. The intensity of the NMR signal is proportional to the number of ^{89}Y nuclei which obey the resonance condition

$$H_0=2\pi\frac{\nu_{rf}-k}{\gamma}-A\langle S_i^z\rangle, \tag{2}$$

where γ is the ^{89}Y-gyromagnetic factor, $A=1.3$ T is the ^{89}Y-Ni^{2+} hyperfine coupling constant in Y_2BaNiO_5 and k is an i-independent factor that accounts for the chemical and orbital shifts. Using Eq. (2), the local magnetization of the open classical chain and the position of the peaks in the NMR spectra can be directly compared. Since k is not known precisely *a priori*, we fix it by matching the spin polarization at the center of the chain with the maximum of the NMR central line.[15] Then, as sketched in Fig. 2, a satellite peak is found in correspondence of each value of magnetization taken by the edge spins.

The magnetization profiles can be analyzed in detail, by observing that $\langle S_i^z\rangle$ consists in a uniform part and of staggered contributions decaying away from each boundary. The following phenomenological function:

$$\langle S_i^z\rangle=\langle S_b^z\rangle+\langle S_1^z\rangle[(-1)^{(i-1)}e^{(i-1)/\xi}+(-1)^{(L-i)}e^{(L-i)/\xi}] \tag{3}$$

is thus used to fit the numerical data. Expression (3) describes very well the behavior of $\langle S_i^z\rangle$ in all the investigated temperature range (see, for instance, solid lines in Fig. 2) and the extracted fitting parameters—$\langle S_b^z\rangle$, $\langle S_1^z\rangle$ and ξ—turn out to be independent of the chain length L. The two alternating terms in Eq. (3) give an in phase (out of phase) contribution in chains with odd (even) number of spins. In real systems, consisting in an ensemble of segments with different length, such effect induces a distribution of $\langle S_i^z\rangle$ and thus a broadening of the NMR satellite peaks, as actually observed in Fig. 2. Here we do not investigate this subject quantitatively, being mainly interested to discuss the behavior of the parameters extracted from the classical Monte Carlo data in light of the values for the same quantities obtained by NMR in the $S=1$ chain.

In Fig. 3(a), the temperature behavior of the uniform term $\langle S_b^z\rangle$ is reported. $\langle S_b^z\rangle$ depends linearly on the field up to 40 T (inset) and follows strictly the magnetization $\chi\cdot H$ that would be obtained by using for χ the zero-field susceptibility of the infinite classical chain[18] [solid line in Fig. 3(a)]. This result should be intuitively expected, since the staggered terms in Eq. (3) involve only boundary spins and thus, in the thermodynamic limit, the ''bulk'' magnetization is due only to $\langle S_b^z\rangle$. The first-site magnitude $\langle S_1^z\rangle$ and the decay length ξ of the staggered contributions, extracted from the simulation, are reported, respectively, in Figs. 3(b) and 4 and compared with the experimental values of $\langle S_1^z\rangle$ and ξ from ^{89}Y NMR in doped Y_2BaNiO_5.[5] The agreement between experimental results in the HAF $S=1$ one-dimensional compound and predictions of the classical model is remarkable at high temperature. Small quantitative deviations, which likely prelude to a more sensible departure at lower temperatures, are ob-

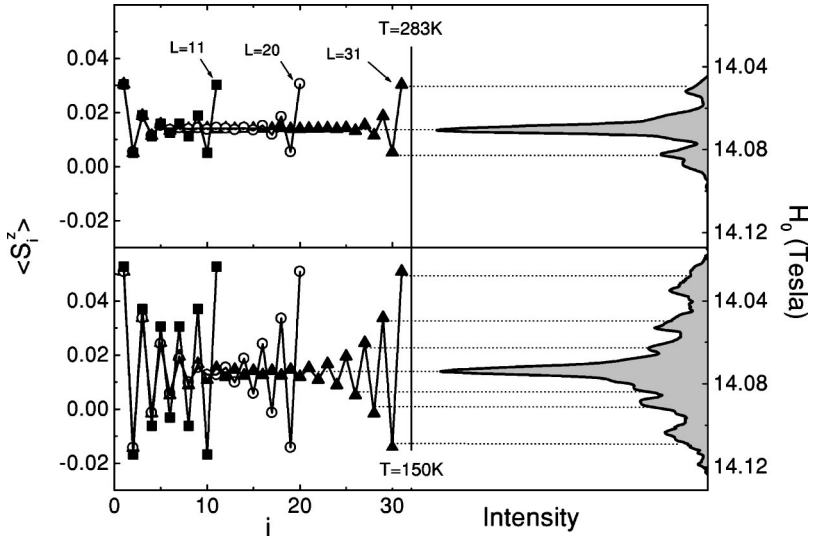

FIG. 2. Left side: magnetization profiles $\langle S_i^z\rangle$ in a field $H=14.1$ T for $S=1$ chains with $J/k_B=285$ K and various lengths (from classical Monte Carlo). Solid lines are fittings of the data according to the phenomenological model described by Eq. (3). On the right side ^{89}Y NMR spectra in doped HAF chain $Y_2BaNi_{1-x}Mg_xO_5$ (from Ref. 5) are reported. Through Eq. (2) in the text, the local magnetization of the classical chain can be quantitatively compared to the NMR spectra of the $S=1$ chain and the correspondence between boundary moments and satellite peaks is directly inferred.

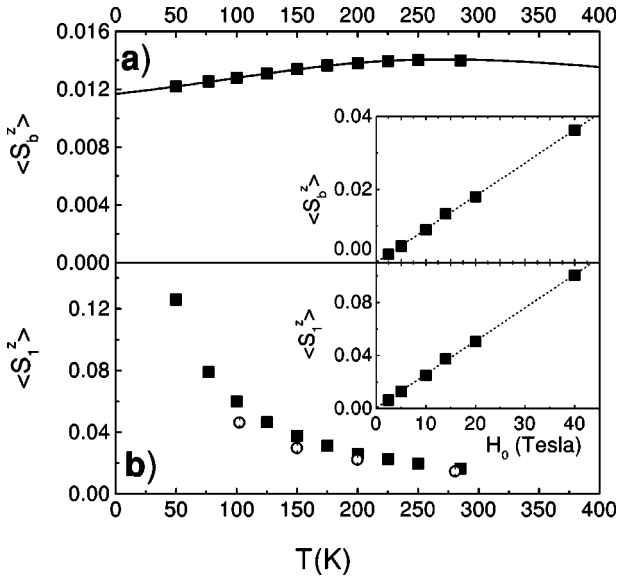

FIG. 3. (a) Temperature behavior of the uniform magnetization $\langle S_b^z \rangle$ in $H=14.1$ T extracted from classical Monte Carlo data by Eq. (3) (full squares). Solid line is the exact classical thermal expectation value of the on-site magnetic moment for a chain with $L \to \infty$, calculated through Fisher's formula for the uniform susceptibility (Ref. 18). (b) The first-site staggered magnetization $\langle S_1^z \rangle$ of the classical chain is compared to the experimental value of $\langle S_1^z \rangle$ measured by NMR in Mg-doped Y_2BaNiO_5 (Ref. 5) (open circles). In the insets it is shown how $\langle S_b^z \rangle$ and $\langle S_1^z \rangle$ depend linearly on the applied magnetic field up to 40 T.

served only around $T=100$ K$\simeq \Delta_H/k_B$. At the moment, the lack of experimental data for $\langle S_1^z \rangle$ and ξ below 100 K (due to the broadening of the NMR lines) prevents a precise definition of the temperature range in which the classical model accounts for the magnetic response of the open $S=1$ chain. Figure 4 also shows how the decay length ξ of the staggered magnetization in a weak external field ($H=14.1$ T) tracks strictly the behavior of the zero-field spin-spin correlation length (solid line), calculated by Fisher[18] for the infinite-volume chain.

In the inset of Fig. 4, the total magnetic moment associated to each staggered contribution,

$$\langle S_T^z \rangle = \sum_{i=1}^{L} \langle S_1^z \rangle (-1)^{(i-1)} e^{(i-1)/\xi}, \tag{4}$$

is plotted as a function of temperature. $\langle S_T^z \rangle$ is well reproduced by a Curie-like law

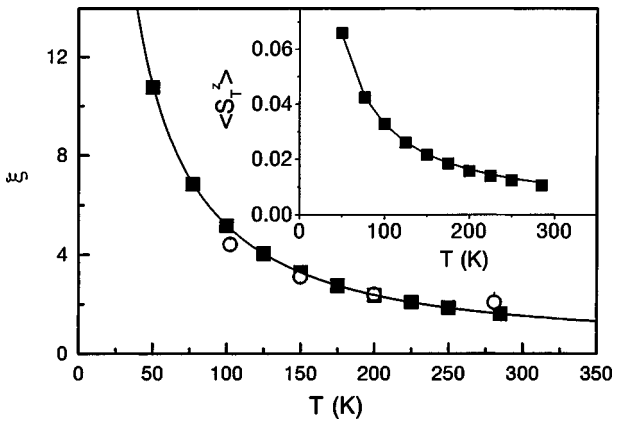

FIG. 4. Decay length ξ of the staggered magnetization, obtained from Monte Carlo calculations through Eq. (3) (full squares), *vis-à-vis* to the experimental values of ξ (open circles)[5] and to the zero field correlation length of the infinite-L classical chain (Ref. 18) (solid line). In inset, the total magnetization $\langle S_T^z \rangle$, associated to one of the chain boundaries [see Eq. (4) in the text], is fitted by the Curie law (5).

$$\langle S_T^z \rangle = \frac{g \mu_B S_f^2 H}{3 k_B T}, \tag{5}$$

characteristic of noninteracting classical moments of magnitude S_f. The value of S_f that optimizes the fitting (solid line in the inset in Fig. 4) is 0.72, about half of the site-spin magnitude $\sqrt{S(S+1)}=\sqrt{2}$. This result extends to a temperature region in which the system shows classical behavior the low-T picture for gapped spin chains, in which $S/2$ degrees of freedom develop at the chain edges.[19,8–11] Moreover, since the temperature dependence of $\langle S_T^z \rangle$ is mainly controlled by $\langle S_1^z \rangle$ for $\Delta_H/k_B \leqslant T \leqslant J/k_B$, even the first-site staggered moment displays approximately a Curie-like behavior.

In summary, our numerical results prove that the alternate boundary magnetization observed experimentally in finite-length $S=1$ HAF chains is correctly predicted, for $\Delta_H/k_B \leqslant T \leqslant J/k_B$, by a strictly classical analysis of the Heisenberg model. In light of this evidence we conclude that the occurrence of Curie-like fractional-spin defects is a general feature in HAF one-dimensional systems with open boundaries, not related to the occurrence of a spin gap. On the other hand, the size of these staggered defects, which is fixed by the bulk spin-spin correlation length, is affected by quantum fluctuations and is thus expected to remain finite when the ground state is spin-liquid like.

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