Coexistence of Haldane-gap excitations and long-range antiferromagnetic order in mixed-spin nickelates R_2BaNiO_5

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The spin dynamics of the $S=1$ Ni chains in mixed-spin antiferromagnets Pr_2BaNiO_5 and $Nd_xY_{2-x}BaNiO_5$ is described in terms of a simple Ginzburg-Landau Lagrangian coupled to the sublattice of rare-earth ions. Within this framework we obtain a theoretical explanation for the experimentally observed coexistence of Haldane-gap excitations and long-range magnetic order, as well as for the increase of the Haldane-gap energy below the Néel point. We also predict that the degeneracy of the Haldane triplet is lifted in the magnetically ordered phase. The growth of both gaps are shown to follow from the magnon repulsion. The theoretical results are consistent with the available experimental data. [S0163-1829(98)07701-7]

Much excitement in the field of low-dimensional quantum magnetism was caused by the theoretical work of Haldane, who predicted an energy gap in the excitation spectrum of a one-dimensional Heisenberg antiferromagnet (1D HAF) with integer spin.[1] At the beginning this came as a surprise, since for the half-integer-spin 1D HAF the excitation spectrum was known to be gapless. Very soon Haldane's conjecture was confirmed by many numerical and experimental studies,[2] and the ''Haldane gap'' phenomenon is by now rather well understood. A very challenging outstanding problem now is to study the *quasi*-1D case, when 3D magnetic interactions are sufficiently strong to destroy the Haldane singlet and produce long-range magnetic order at low temperature, yet some purely quantum-mechanical effects are preserved, thanks to the dominance of 1D interactions. Much experimental and theoretical work in this direction was done on $CsNiCl_3$ (Ref. 3) and isostructural integer-spin compounds.[4] The result was a profound understanding of the connection that exists between Haldane excitations and ''normal'' spin waves. In $CsNiCl_3$ for example, the triplet of 1D Haldane gap modes is readily observed above the Néel temperature T_N. As T_N is approached from above, the gap vanishes at the 3D magnetic zone center, driving a soft-mode transition. In the ordered phase two of the three modes become conventional gapless spin waves, while the third ''longitudinal'' mode, not accounted for by the linear spin-wave theory, persists as a gapped excitation.

Recently in a series of inelastic neutron-scattering studies of quasi-1D mixed-spin antiferromagnets with the general formula R_2BaNiO_5 (R=Pr, Nd or Nd_xY_{1-x}) Zheludev *et al.*[5] demonstrated that the scenario realized in $CsNiCl_3$ is by no means universal. In R_2BaNiO_5 compounds 3D magnetic ordering produces finite static moments on both the $S=1$ Ni^{2+} and the R^{3+} magnetic ions,[6] yet the 1D gap excitations propagating on the Ni chains are only weakly affected: they persist in the ordered phase as gapped modes and *coexist* with conventional acoustic spin waves all the way down to $T=0$. These excitations show no signs of softening at the transition point at any wave vector. In the entire phase diagram they have a purely 1D dynamic structure factor that is practically indistinguishable from that of Haldane excitations in Y_2BaNiO_5,[7] a ''clean'' Haldane-gap material, where only the Ni sites are magnetic, and no long-range ordering occurs. In R_2BaNiO_5 the only significant (and rather unexpected) effect of 3D ordering is that the gap energy *increases* in the ordered phase, the increase being roughly linear with (T_N-T). The survival of 1D quantum spin excitations in the ordered state is indeed remarkable since the transition temperatures are rather high, and are quite comparable to the gap energy. The purpose of this letter is to explain the coexistence of long-range order and Haldane-gap excitations in R_2BaNiO_5 materials. We propose that, contrary to the case of $CsNiCl_3$, in these compounds Ni chains do not interact between themselves, but instead each is coupled to the sublattice of magnetic R ions. We derive the experimentally observed growth of the gap below T_N using a simple Ginzburg-Landau Lagrangian.[8] In addition, we predict that the degeneracy of the Haldane excitations is partially removed in the ordered phase and notice an intriguing analogy between this gap splitting in R_2BaNiO_5 materials and the famous Higgs mechanism of lifting the mass degeneracy in particle physics.

Integer spin chains are traditionally described in terms of the Lagrangian of the nonlinear sigma model (NLSM). In this approach one approximates the field of spin site operators $\vec{S}_i$ $[\vec{S}_i^2=s(s+1)]$, retaining only the Fourier components near $k_x=0$, and π.[1] This is accomplished by a change in real space variables

$$\vec{S}_i=s(-1)^i\vec{\varphi}(i)+\vec{l}(i), \tag{1}$$

where both fields $\vec{\varphi}(i)$, and $\vec{l}(i)$ change *slowly* on the scale of one lattice spacing. According to this definition, $\vec{\varphi}(i)$ is the unit vector in the direction of local staggered magnetization, and $\vec{l}(i)$ is the component of local magnetization perpendicular to $\vec{\varphi}(i)$ $(\vec{\varphi}(i)\cdot\vec{l}(i)=0)$. In the limit of large s three components of $\vec{\varphi}$ commute with each other, while the commutation rules of $\vec{l}$ remain nontrivial. It can be shown that the correct dynamics for the new variables follows from a NLSM Lagrangian:

$$\mathcal{L}=\frac{1}{2g}\int dx\left[\frac{1}{v}\left(\frac{\partial\vec{\varphi}}{\partial t}\right)^2-v\left(\frac{\partial\vec{\varphi}}{\partial x}\right)^2\right], \quad (2)$$

where $\vec{\varphi}$ is subject to the constraint $\vec{\varphi}^2=1$. Here $g=2/s$ is a dimensionless coupling constant, measuring the strength of quantum fluctuations, and $v=2Js$ is the spin-wave velocity. The magnetic moment $\vec{l}$ is given by $\vec{l}=1/gv\ \ \vec{\varphi}\times\partial\vec{\varphi}/\partial t$. This mapping of the 1D HAF to the NLSM (2) becomes exact for integer $s\to\infty$, but it gives a meaningful and qualitatively correct approximation even for $s=1$. From this description it can be derived that in $1+1$ dimensions any strength of quantum fluctuations g is sufficient to destroy long-range correlations between spins. A finite correlation length ξ is always accompanied by a gap $\Delta=v/\xi$ in the spin-excitation spectrum. For half-integer 1D HAF the topological term not included in the Lagrangian (2) prevents the appearance of the finite correlation length, and spin correlations remain scale free. But for integer s this gap, commonly known as the Haldane gap, is present. It has small g (large s) asymptotics of $\Delta\sim v\exp(-2\pi/g)=v\exp(-\pi s)$. For the $s=1$ HAF the Haldane gap was found numerically to be $\Delta=0.41J$.[9]

The nonlinear sigma model is not very convenient for practical calculations. To simplify things further we follow the approach of Affleck,[8] and replace the Lagrangian of NLSM with that of the quantum Ginzburg-Landau model

$$\mathcal{L}=\int dx\left[\frac{1}{2v}\left(\frac{\partial\vec{\phi}}{\partial t}\right)^2-\frac{v}{2}\left(\frac{\partial\vec{\phi}}{\partial x}\right)^2-\frac{\Delta^2}{2v}\vec{\phi}^2-\lambda|\vec{\phi}|^4\right], \quad (3)$$

where for convenience we have simultaneously changed variables to $\vec{\phi}=1/\sqrt{g}\,\vec{\varphi}=\sqrt{s/2}\,\vec{\varphi}$. The new Lagrangian follows from Eq. (2) if the constraint $\vec{\varphi}^2=1$ is relaxed, making the vector of staggered magnetization soft, and phenomenological quadratic and quartic terms are introduced. The coefficient in front of the quadratic term is selected to reproduce the correct value of the gap (in NLSM this gap is generated dynamically), while the only condition imposed on the quartic term is that $\lambda>0$, ensuring the overall stability for large $|\vec{\phi}|$. The physical meaning of Eq. (3) is rather transparent. It describes the propagation of a triplet of magnons (excitations of local staggered magnetization) with a given spin-wave velocity v, and gap Δ. The quartic term describes the repulsive magnon-magnon interaction.

The Lagrangian (3) was successfully used to qualitatively explain the behavior of coupled 1D spin chains in $CsNiCl_3$.[8] In this case the ith chain is described by Eq. (3) with $\vec{\phi}\to\vec{\phi}_i$, while the interchain coupling is given by $-2sJ'\vec{\phi}_i\cdot\vec{\phi}_{i+1}$. On the mean-field level the behavior of the excitations is the following: the gap is reduced by the interchain coupling to $\Delta_{\rm eff}^2=\Delta^2(T)-4vZsJ'$, where Z is the number of chains coupled to a given chain. The $O(3)$ symmetry is spontaneously broken for $\Delta^2(T)<4ZsvJ'$. In this case $|\vec{\phi}|$ has a nonzero expectation value of $\sqrt{[4vZsJ'-\Delta^2(T)]/4v\lambda}$. The gap naturally grows with temperature and eventually wins over the interchain exchange, restoring the $O(3)$ symmetry. The Néel temperature is determined by the condition $\Delta^2(T_N)=4vZsJ'$. It is important to understand what happens to the triplet of magnons below T_N. As T_N is approached from above, the gap in all three excitations at the positions of future magnetic Bragg peaks decreases and hits zero at T_N. Below T_N two excitations corresponding to the two Goldstone modes of the Néel order parameter remain gapless. At the same time the longitudinal branch reacquires the gap along with a finite lifetime due to decay into two gapless modes.

The ''traditional'' scenario[8] described above is in agreement with experimental findings in $CsNiCl_3$. However, for R_2BaNiO_5 we can expect a different picture. The structure of these materials is such that there are no strong direct superexchange paths between the Ni chains, which explains why in isostructural Y_2BaNiO_5 no magnetic ordering is observed.[7] On the other hand, magnetic rare-earth ions substituted for Y are coupled between themselves. To a good approximation one can assume that these sites form a separate sublattice which orders at rather high temperatures ($T_N=48$ K for Nd_2BaNiO_5). The coupling J' between the Ni and R sublattices is weak, yet finite. The finite ordered moments on the Ni sites may be interpreted as the singlet-ground-state Ni chains being *polarized* by a staggered exchange field from the magnetically ordered sublattice of R ions. To describe this effect an ''external field'' term should be added to the Ginzburg-Landau Lagrangian (3). It is given by $J'\vec{n}\cdot\sqrt{2s}\,\vec{\phi}=\vec{H}_s\cdot\vec{\phi}$, where $\vec{n}$ is the staggered moment of the R sublattice. Such a term explicitly breaks the $O(3)$ symmetry and causes $\vec{\phi}$ to acquire a nonzero expectation value along $\vec{H}_s$. As a consequence, the degeneracy of the triplet of Haldane-gap excitations is partially lifted. The energy gap in the magnon, polarized parallel to $\vec{H}_s$, is different from that in the two transversal branches. Both gaps can be derived from $\mathcal{P}$ — the potential energy density of the Lagrangian:

$$\mathcal{P}=\frac{1}{2v}\left(\frac{\partial\vec{\phi}}{\partial x}\right)^2+\frac{\Delta^2}{2v}\vec{\phi}^2+\lambda|\vec{\phi}|^4-\vec{H}_s\vec{\phi}. \quad (4)$$

The usual formula for this is $\Delta_\alpha^2/v=\partial^2\mathcal{P}/\partial\phi_\alpha^2$. It gives

$$\Delta_{||}^2=\Delta_0^2+12v\lambda\phi_0^2,$$
$$\Delta_\perp^2=\Delta_0^2+4v\lambda\phi_0^2. \quad (5)$$

Here ϕ_0 is the expectation value of $|\vec{\phi}|$ determined by minimization of Eq. (4) through

$$H_s=\Delta_0^2/v\,\phi_0+4\lambda\phi_0^3, \quad (6)$$

or, approximately, $\phi_0\simeq vH_s/\Delta_0^2$. Note that both energy gaps are increased compared to their value in the absence of the staggered field. This observation relies on the fact that $\lambda>0$, i.e., a repulsive magnon-magnon interaction. It is precisely the positive λ, which guarantees the stability of Eq. (6) and of the Lagrangian (3) itself, and, therefore, should be satisfied.

As we mentioned in the introduction, the Lagrangian of NLSM is traditionally used to describe the behavior of quantum spin chains. The effect of the staggered magnetic field in NLSM, coupled to the staggered magnetization via the term $\vec{n}\cdot\vec{h}/g$, was studied by Nelson and Pelcovits[10] using renormalization-group methods. Their RG flow indicates that indeed the gap increases (the correlation length decreases) in

strong enough fields. The one-loop corrections calculated by them do not give a definite answer about the behavior of the correlation length in weak fields. Using our results for the Ginzburg-Landau Lagrangian we can conclude that the correlation length decreases in this case as well.

Our predictions for the energy gap can be qualitatively understood by working with the original Heisenberg Hamiltonian and treating the staggered field as a weak perturbation. Let us denote the Haldane ground state by $|G\rangle$ and label the lowest-energy triplet excitations at $q=\pi$ as $|E,+1\rangle$, $|E,0\rangle$ and $|E,-1\rangle$, according to their value of S_z. Let us now consider the relevant matrix elements of the staggered field operator $\hat{H}_s=H_s\Sigma_j(-1)^j S_j^z$. These are nonzero only between states with momentums differing by exactly π. In particular, $\langle G|\hat{H}_s|G\rangle$, as well as the matrix elements between any two of the $|E,+1\rangle$, $|E,0\rangle$ or $|E,-1\rangle$ states are strictly zero. As a result, there are no first-order corrections to the spin gap at $q=\pi$. To calculate the second-order correction δE_G to the ground-state energy we can use the well-known fact that the triplet of Haldane modes pretty much exhausts the spectral weight at $q=\pi$. Thus, only the mixing of $|G\rangle$ with single-particle excitations needs to be considered. Since $\hat{H}_s$ conserves the z component of the total spin, its only nonzero matrix element is the one between $|G\rangle$ and $|E,0\rangle$. The correction to the ground-state energy is thus given by $\delta E_G=-|\langle E,0|\hat{H}_s|G\rangle|^2/\Delta\equiv-\epsilon$. We now proceed to calculate the energy corrections for the three excited states at $q=\pi$. Two effects need to be considered: (i) their mixing with the ground state and (ii) their mixing with two-particle excited states. Let us first assume that there is no repulsion between magnons, and that doubly excited states at $q=0$, which we label as $|2E,+1,0\rangle$, $|2E,-1,0\rangle$, and $|2E,0,0\rangle$, are produced by adding two noninteracting $q=\pi$ excitations (bosons) to the system. Second-order corrections to the energies of singly-excited states are then given by

$$\delta E_{E,0}=\frac{|\langle G|\hat{H}_s|E,0\rangle|^2}{\Delta}-2\frac{|\langle 2E,0,0|\hat{H}_s|E,0\rangle|^2}{\Delta}$$

$$=\epsilon-2\epsilon=-t$$

and

$$\delta E_{E,+1}=-\frac{|\langle 2E,+1,0|\hat{H}_s|E,+1\rangle|^2}{\Delta}=-\epsilon=\delta E_{E,-1}.$$

The correction to the gap energies then become *zero*. Magnon repulsion effectively reduces the negative second-order corrections to the single-particle excitation energies that are due to mixing with double-excited states. This will lead to an *increase* of the gap energy. Both $\Delta_\perp$ and $\Delta_\parallel$ will increase quadratically with H_s, though for $\Delta_\parallel$ the effect in general may be more pronounced. This is totally consistent with results derived above, where the positive parameter λ represents repulsive interactions between magnons.

An increase of the energy gap below the transition point is exactly what was observed in neutron-scattering experiments on Nd_2BaNiO_5, $Nd_xY_{2-x}BaNiO_5$, and Pr_2BaNiO_5.[5] The data were taken on powder samples or single crystals of small size, which obviously made resolving the mode splitting below T_N impossible. In the powder measurements at least, the observed gap always corresponds to the lowest-energy mode.

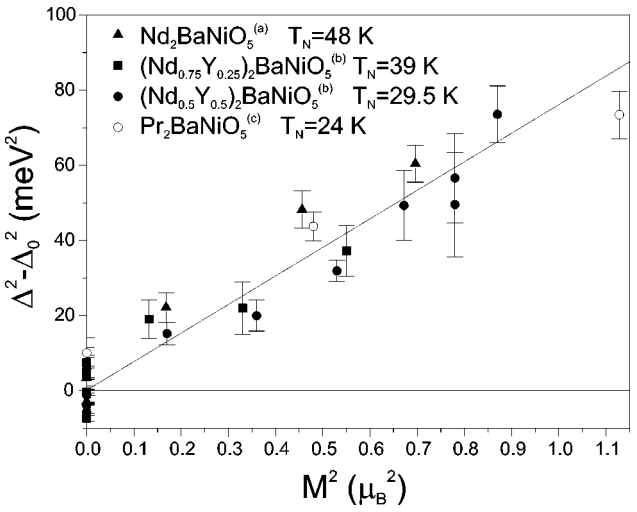

FIG. 1. Experimentally measured increase of the square of the gap energy in R_2BaNiO_5 samples relative to that in Y_2BaNiO_5 at the same temperature, plotted against the square of staggered magnetization of Ni sites.

In Fig. 1 we show the combined data from all experiments, plotting the increase of the square of gap energy [relative to that measured in Y_2BaNiO_5 (Ref. 11) at the same temperature] against the square of staggered magnetization of the Ni sublattice. The data are consistent with the predicted linear dependence. Moreover, data points for different compounds seem to collapse onto a single curve, even though the Néel temperatures vary considerably. The mechanism is therefore insensitive to the details of exchange in the *R* sublattice, and between Ni and *R* sublattices.

In a much obscured form the effect of the staggered field has been previously observed in the well-known Haldane-gap material NENP.[12] In this compound applying an external *uniform* field H produces a weak effective staggered component due to some special structural features. On top of a very pronounced linear splitting of the Haldane triplet by the uniform field for each mode one observes a slight energy shift that is *positive* and quadratic with H. This shift was attributed to the weak staggered field component that for NENP is inseparable from the uniform one.[13] Numerical calculations have confirmed this conclusion.[14] Note that unlike in NENP, in R_2BaNiO_5 systems we are able to see the effect of the staggered field much more clearly, since the dominant uniform field component is absent.

It is interesting to mention that the effect of gap increase and splitting due to interaction with another sublattice has a close analog in the field of particle physics. It is very similar to the Higgs mechanism by which the mass degeneracy in a multiplet of elementary particles is lifted. As in our case, the splitting of masses (energy gaps relative to a vacuum of particles) is a result of spontaneous symmetry breaking, produced by the interaction with Higgs particles. The three Ni chain Haldane excitations of different polarizations play the role of a multiplet of particles of initially equal masses, while the conventional acoustic spin waves, referred to as mixed *R*-Ni excitations by Zheludev *et al.*, play the role of the elusive Higgs particle, which is massless in our case. This analogy should not be taken too seriously due to the differences in Hamiltonians: it is the SU(2) symmetry which is sponta-

neously broken by the Higgs mechanism, and the term describing the coupling between matter and Higgs particles is more complicated than a simple $-\vec{H}_s\vec{\phi}$ term in our case. Nevertheless, the essence of the effect is the same: spontaneous symmetry breaking caused by interaction with some external field lifts the degeneracy of masses (gaps).

In conclusion, we have provided a simple theoretical explanation for the coexistence of long-range magnetic order and Haldane-gap excitations in R_2BaNiO_5 systems. The Ni-chain gap modes are described in terms of a simple Ginzburg-Landau Lagrangian. The increase of the gap below the Néel temperature, previously observed experimentally in several compounds, immediately follows from this approach. The qualitatively new prediction is that the degeneracy of the Haldane triplet is lifted below the transition point. The magnon polarized along the vector of staggered magnetization has a larger gap than the two others magnon branches. Experimental tests of this prediction, including inelastic neutron-scattering experiments on large high-quality single samples, are planned for the near future.

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