PHYSICAL REVIEW B **82**, 100407(R) (2010)

Magnetic-field-induced phase transition of coupled edge spins in the Haldane gap system $Y_2BaNi_{1-y}Mg_yO_5$

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(Received 18 August 2010; published 9 September 2010)

A magnetic phase transition is induced by magnetic field in a Haldane gap system $Y_2BaNi_{1-y}Mg_yO_5$, where nonmagnetic Mg dopants cut an infinite chain into finite segments randomly. The ordering is realized only for field direction parallel to the c axis and above a critical field $\mu_0 H_c \sim 2$ T, which is much smaller than the Haldane gap of Y_2BaNiO_5 (~ 70 T). The phenomenon is correlated with the field-induced energy-level crossing of the eigenstates for coupled edge spins at both ends of each segment. Although the crossing field depends on the length of the segments, macroscopic ordering is realized.

DOI: 10.1103/PhysRevB.82.100407 PACS number(s): 75.45.+j, 75.40.Cx, 75.90.+w

Field-induced phase transition in spin singlet system has been studied intensively for a decade.[1,2] The dominant interaction is antiferromagnetic (AFM) within singlet pair (intrapair interaction J). At zero-field, spin gap separates the singlet and the triplet states. With increasing the field, the energy of one of the triplet states decreases by Zeeman energy and eventually the gap closes (energy-level crossing).[3] Around the crossing field, the wave functions of the ground and the first excited states are mixed macroscopically by the exchange interaction J' that works between singlet pairs (interpair interaction), and the magnetic ordering is realized.[4,5] For a spin dimer system $TlCuCl_3$, $J'/J \sim 0.27$.[6] Similar field-induced transition is reported for an $S=1$ system,[7,8] where a pair of $S=1/2$ spins in an identical ion is coupled ferromagnetically (FM) by the Hund's coupling. The single-ion anisotropy opens spin gap between the triplet states, and the level crossing occurs between these states by application of magnetic field for a restricted field direction. J' induces ordering as well.

We present field-induced transition in an impurity-doped Haldane gap system $Y_2BaNi_{1-y}Mg_yO_5$ ($y=0.04$). The parent compound Y_2BaNiO_5 consists of $S=1$ Heisenberg AFM chains running along the a axis with spin gap (Haldane gap) $\Delta \sim 8.6$ meV.[9] By the substitution of nonmagnetic Mg for Ni ions, infinite chains are cut into finite chain segments. Since the Haldane gap is robust against Mg substitution, two $S=1/2$ edge spins appear at both ends of segments.[10–13] Due to the exchange interaction between the edge spins within each segment and single-ion anisotropy, four eigenstates (singlet and triplet states) of the coupled edge spins appear inside the Haldane gap.[12,13]

Single crystals of $Y_2BaNi_{1-y}Mg_yO_5$ ($y=0.04$) were grown using the traveling solvent floating zone method.[14] Specific-heat measurements were performed using the thermal-relaxation method in a He3 refrigerator. The spin specific heat $C_{spin}(T)$ was obtained by subtracting the specific heat of Y_2BaNiO_5 from the measured whole specific heat. The specific heat of Y_2BaNiO_5 is a good approximation of the lattice contribution in a temperature range much lower than the Haldane gap (~ 100 K). The direction of the magnetic field relative to a crystal was rotated manually.

When magnetic fields were applied parallel to the c axis, an anomaly was observed in $C_{spin}(T)/T$, as shown in Fig. 1(a). For $\mu_0 H=3$ T, $C_{spin}(T)/T$ shows lambda-shaped jump at $T=0.8$ K, revealing the presence of second-order phase transition. No hysteresis was observed. The anomaly is superimposed on Schottky anomalylike background, which is characteristic of the doped samples and originates from the thermal excitation of the edge spin states. The transition temperature increases with increasing the field. At high fields, although the jump is not so clear, the slope of $C_{spin}(T)/T$ is discontinuous at the transition. The anomaly was reproducible using other crystals. The spin entropy in the temperature range up to 20 K is ~ 0.40 J/mol K, which is close to 0.46 J/mol K expected for $y=0.04$ on the assumption that each Mg ion induces two $S=1/2$ edge spins, revealing that edge spins play an important role at low temperatures.[11] $C_{spin}(T)/T$ at low temperatures obeys a power law rather than an exponential law, as is displayed by nearly linear lines in logarithmic plots (not shown). It implies gapless excitation in the ordered phase, as was observed in $TlCuCl_3$.[3] No such anomaly was observed for $H \| a$ or b, as shown in Fig. 2(b).

The transition is extremely sensitive to the field direction. In Fig. 2(a), $C_{spin}(T)/T$ for various field directions is plotted. With increasing the angle from the c axis, the transition temperature increases and the transition width becomes broader, and eventually the curve crosses over to Schottky anomaly-like behavior. For the negative angles, nearly symmetric behavior was observed. The ordering exists in a very narrow range of $\sim 1°$, which shows that the phenomenon is governed not by the field component parallel to the c axis but by the field direction itself, and that the transition is intrinsic to the compound. The spin entropy seems conserved during this crossover, which is evidence that the degree of the freedom of the edge spins but not others are involved in the ordering.

The phase diagram obtained from the jump in Fig. 1(a) is shown in Fig. 1(b). The phase boundary can be approximated by a linear line of $k_B T_c \sim \mu_B (H - H_c)$, which implies that the transition is governed by the Zeeman energy and is magnetic, where μ_B is Bohr magneton and k_B Boltzmann constant. At zero field, the compound is nonmagnetic down to $T=50$ mK.[10] Therefore, the left-handed phase is paramagnetic

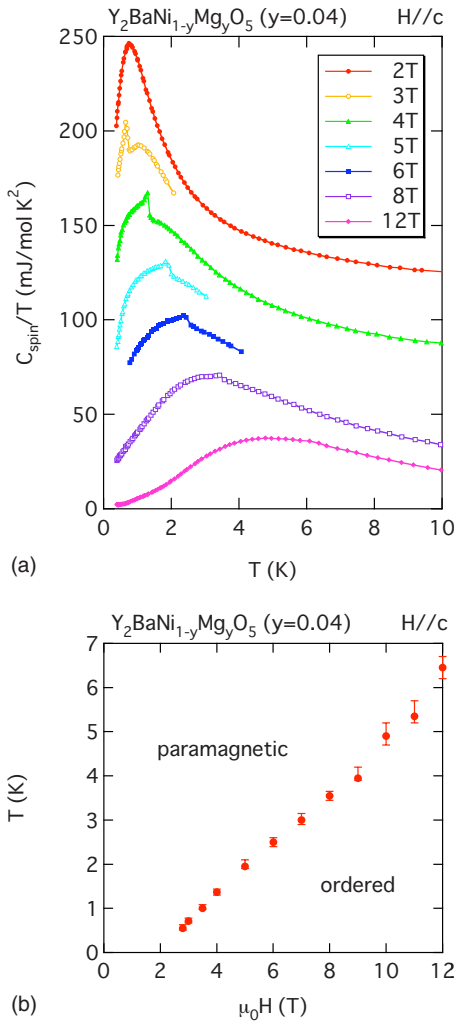

FIG. 1. (Color online) (a) The temperature dependence of C_{spin}/T of $Y_2BaNi_{1-y}Mg_yO_5$ (y=0.04) under various magnetic fields parallel to the c axis. Each data set is shifted upward one by one with an offset of 20 mJ/mol K^2. (b) The phase diagram of $Y_2BaNi_{1-y}Mg_yO_5$ (y=0.04) under the magnetic fields parallel to the c axis, obtained from the specific-heat anomaly. Each point and its error bars are defined by the temperatures where C_{spin}/T is at the half of the jump and where C_{spin}/T is at the top and the bottom of the jump, respectively.

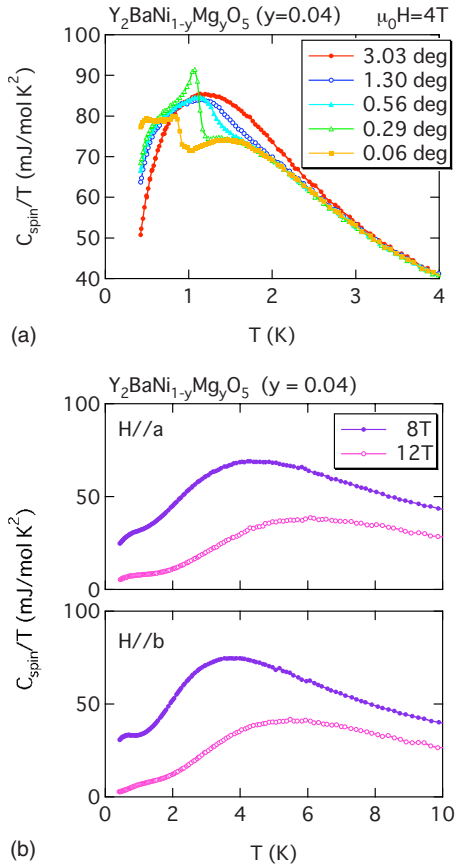

FIG. 2. (Color online) (a) The temperature dependence of C_{spin}/T of $Y_2BaNi_{1-y}Mg_yO_5$ (y=0.04) at the magnetic field of 4 T. The field is applied parallel to the ac plane and the angle in the legend is between c axis and the field direction. Different sample from that in Fig. 1(b) was used. Possible discrepancy of the data between these samples may be due to misalignment for the sample setting and/or imperfectly aligned crystal domains. (b) The temperature dependence of C_{spin}/T of $Y_2BaNi_{1-y}Mg_yO_5$ (y=0.04) at low temperatures for $H\|a$ and b axes. The data sets for μ_0H=8 T are shifted upward by 20 mJ/mol K^2.

and the right-handed one is magnetically ordered. By the extrapolation with the linear line, the critical field μ_0H_c is ~2 T. It is quite small compared to the estimated critical field of the parent compound Y_2BaNiO_5 ($\Delta/g\mu_B \sim 70$ T), where the Haldane gap is expected to collapse. The edge spins with smaller energy scale is likely to order.

The phase transition in $Y_2BaNi_{1-y}Mg_yO_5$ seems different from impurity-induced phase transition[15,16] and rather similar to field-induced one. In the former type, an ordered phase exists at zero field and the field tends to suppress the transition temperature.[17–19] In the latter, on the other hand, an ordered phase does not exist at zero field and is induced by field, and further field enhances the transition temperature. In the latter, spin pair such as the spin dimer in $TlCuCl_3$ is necessary for the ordering. For $Y_2BaNi_{1-y}Mg_yO_5$, the edge spins at both ends of a segment are coupled[13] and can be considered as a spin pair. In this picture, the system consists of edge spin pairs that cover the entire system. Since the level crossing and the mixing of the wave functions may be expected for the edge spin pairs, we survey their energy diagrams.

By the diagonalization of an effective Hamiltonian of segments with the chain length (the number of Ni sites) N,[13,20] we obtained their energy diagrams as in Fig. 3. In a segment with even N (even chain), J is AFM, and the level crossing occurs between singlet and triplet states for any field direction, as in the spin singlet systems.[3,4] (See the upper part of Fig. 3.) In a segment with odd N (odd chain), J is FM and single-ion anisotropy in a form of $Ds_a^2+E(s_b^2-s_c^2)$ (Ref. 9) opens spin gap between triplet states, where single-ion parameters D and E depend on N. The level crossing occurs between them only for $H\|c$, as in the S=1 system.[7,8] (See the lower part.) This is the field direction where the field-induced phase transition was observed,[21] which suggests that the level crossing in the odd chains plays an important role in the transition. We note that the level crossing in both of the odd

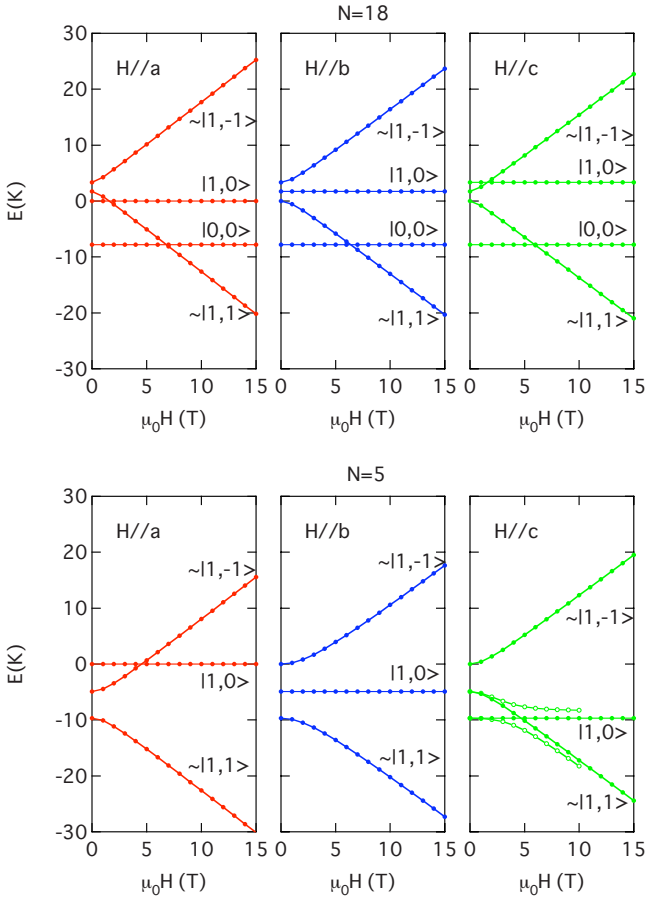

FIG. 3. (Color online) Calculated energy diagram of the edge spin pairs as a function of magnetic field parallel to the three crystallographic axes, for representative finite chain segments with the length N of 18 (the upper panels) and 5 (the lower panels). The dominant character of the wave function for each branch is shown in a form of $|S,S_z\rangle$. In the lower panels, the energy level of the singlet state is high and beyond the vertical range of the plots. The diagram of the lowest and the second lowest branches of $N=5$ for the field rotated by 20° from the c to the a axis directions is also shown in the lower right panel by open circles.

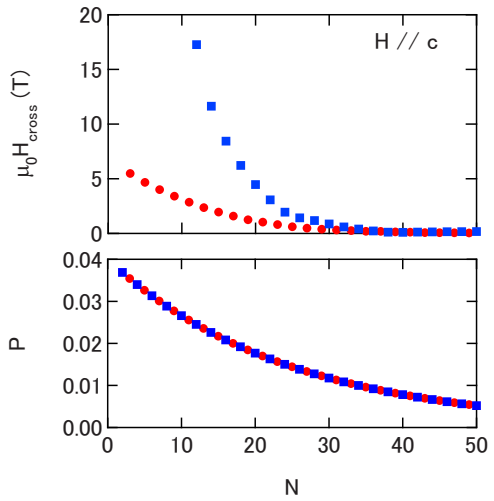

FIG. 4. (Color online) Calculated crossing field $\mu_0 H_{\rm cross}$ for $H\|c$ (the upper panel) and existing probability P (the lower panel) of the chain segment plotted as a function of its length N. Circles and squares depict odd and even chains, respectively. The existing probability of the chain segment with length of N is described by the geometric distribution $y(1-y)^N$, where y is Mg concentration ($y=0.04$).

and the even chains is realized for $H\|c$. The energy scale of the spin excitation of the spin pairs is much smaller than the Haldane gap.

Figure 4 show the N dependence of the crossing field $H_{\rm cross}$ for $H\|c$ and the existing probability P. We assume random distribution of Mg ions. With increasing N, $H_{\rm cross}$ decreases. $H_{\rm cross}$ for the odd chains is much lower than that for the even chains with nearly the same N. From the distribution of $H_{\rm cross}$ and P in the figure, we notice that ~64% of the segments experience the level crossing in a field region below 5 T (around $\mu_0 H_c \sim 2$ T).

For the ordering, moderate J' compared to J is inevitable. We estimate average J and J' for $Y_2BaNi_{1-y}Mg_yO_5$ ($y=0.04$). The effective J ($J_{\rm eff}$) is approximated in the form of $\sim J_o \exp[-(N-2)/\xi]$,[22] where J_o is the bare exchange interaction between the adjacent Ni spins and ξ the correlation length ($\xi \sim 6$).[22] For a segment with the average length $N=24$ corresponding to $y=0.04$, $J_{\rm eff} \sim 0.03 J_o$, which would be a good estimate of average J. Since the paired state for the chain with the length up to 27 is clearly observed in electron spin resonance,[13] $J_{\rm eff} \sim 0.02 J_o$ for $N=27$ should be larger than average J'. It is reported that J' perpendicular to the chain direction in the parent compound Y_2BaNiO_5 is $<10^{-3} J_o$,[9] which would be smaller than J' averaged over every direction, judging from the large spatial separation between the chains. Therefore, average J'/J is expected (slightly) less than unity. Although field-induced transition in such a system is beyond our expectation, it may be possible that the moderate J' induce the ordering. Since the edge spin state spreads with exponential decay of alternating moments from the edge,[22] it would be possible for the ordered moments to percolate throughout the crystal.

It is noticed that small peaks appear at low temperatures in $C_{\rm spin}(T)/T$ for $H\|a$ and b, which is likely to reflect Schottky anomaly of the segments with $H_{\rm cross}$ close to the applied field and to indicate that no macroscopic mixing occurs and the local eigenstates in the segments survive [see Fig. 2(b)]. The small peaks for $\mu_0 H=8$ T are assigned as $N=16$ and/or 18 (the upper panel of Fig. 3) and those for $\mu_0 H=12$ T as $N=14$. In $C_{\rm spin}(T)/T$ for $H\|c$, on the other hand, no small peaks are observed at all, which can be evidence that the macroscopic mixing of the coupled edge spin states occurs due to the ordering [see Fig. 1(a)].

When the magnetic-field direction is rotated from the c-axis direction for the odd chain, the ground and the first excited states are mixed locally within the spin pair (not macroscopically) and split into two levels around the crossing, as shown in Fig. 3. The splitting becomes larger with increasing the angle. The level splitting would transform the phase transition into a crossover. Similar crossover is observed for $S=1$ system with single-ion anisotropy, where the crossover disappears at the rotation angle of 55°.[8] The extreme sensitivity to the rotation angle in $Y_2BaNi_{1-y}Mg_yO_5$ may be related to a subtle combination of the wave functions

of the edge spin pairs with various H_{cross} values that could be easily broken by the level splitting.

In summary, the field-induced transition from nonmagnetic to magnetically ordered states, in $Y_2BaNi_{1-y}Mg_yO_5$ with random intrapair interactions depending on the length of the finite chain segment, is observed. The transition in this system has similar characteristic features to those for a system with uniform exchange interactions between equivalent paired spins, such as $TlCuCl_3$. Moderate interpair interactions compared to intrapair interactions exist. The transition is quite sensitive to the magnetic-field direction. All of these features could originate from the energy-level crossing of eigenstates of finite chain segments.

The authors would like to acknowledge fruitful discussions with M. Matsumoto, C. Broholm, G. Xu, H. Ohta, and S. Okubo.

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