Muon Spin Relaxation and Magnetic Susceptibility Measurements in the Haldane System $(Y_{2-x}Ca_x)Ba(Ni_{1-y}Mg_y)O_5$

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We have performed dc magnetic susceptibility (χ) and muon spin relaxation (μSR) measurements of the Haldane system $(Y_{2-x}Ca_x)Ba(Ni_{1-y}Mg_y)O_5$, in which the chain length is controlled by Ca^{2+} and/or Mg^{2+} doping. In the nominally pure system ($x = y = 0$), we confirmed the absence of static magnetic order down to 100 mK. Similarly, the Mg doped systems ($y = 1.7\%$ and 4.1%) stay paramagnetic down to 50 mK. In the Ca doped systems ($x = 9.5\%$ and 14.9%), the doping-induced unpaired moments exhibit a spin-glass-like cusp in χ, but μSR has revealed spin fluctuations persisting at 50 mK, suggesting an unconventional ground state.

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The ground state properties of a linear chain of antiferromagnetically coupled spins have been a major topic in the study of low dimensional magnetism. Haldane predicted [1] the existence of a large gap between the many-body singlet ground state and the triplet first excited state in an integer spin system with Heisenberg interactions. This conjecture ignited experiments searching for the "Haldane gap" in quasi-one-dimensional spin systems; magnetization and specific-heat measurements have confirmed the existence of the gap [2]. A more direct experimental test is to look for a spontaneous magnetic field in the ground state. If Haldane's conjecture is true, there should be none, reflecting the singlet nature of the ground state. Among various microscopic magnetic probes, muon spin relaxation (μSR) is the most suitable for the possible internal-field search, because (1) the q dependence of the system is integrated in the measurement and (2) μSR has the highest sensitivity to dilute and/or small magnetic moments. There have been μSR experiments on several Haldane materials, including NENP [3] and $AgVP_2S_6$ [4], with the same motivation. These experiments could not detect a static magnetic order for the ground state.

As a model material, we have chosen Y_2BaNiO_5, which is a relatively new Haldane system [5]. In this system, the chain length is easily controlled by doping [6], and the large Haldane gap ($E_g \sim 100$ K) [7–9] makes it easier to measure the ground state properties. Using μSR on doped systems, one can investigate the dynamics of the doping-induced unpaired spins which are embedded in the many-body singlet ground state. In Y_2BaNiO_5, there are two ways to control the chain length: one is *off-chain* charge doping ($Y^{3+} \rightarrow Ca^{2+}$) [10] and the other is *on-chain* site substitution [$Ni^{2+}(S = 1) \rightarrow Mg^{2+}(S = 0)$]. We have found that the two different ways of doping result in completely different magnetic behavior of the doping-induced unpaired spins.

Polycrystalline specimens of nominally pure Y_2BaNiO_5, Ca doped [$(Y_{2-x}Ca_x)BaNiO_5$; $x = 4.5\%$, 9.5%, and 14.9%] and Mg doped systems [$Y_2Ba(Ni_{1-y}Mg_y)O_5$; $y = 1.7\%$ and 4.1%] were prepared at the University of Tokyo, using a standard solid state reaction. Powder x-ray analysis could not detect any impurity phases. We characterized the Ca and Mg concentrations with the atomic light-absorption method.

In Fig. 1, we show the dc magnetic susceptibilities of our specimens. The increase of susceptibility at low temperatures indicates the existence of paramagnetic moments; their amount is related to the doping concentrations (x and y). We analyzed the paramagnetic region of the susceptibilities with the Curie-Weiss law $\chi(T) \approx C/(T +$

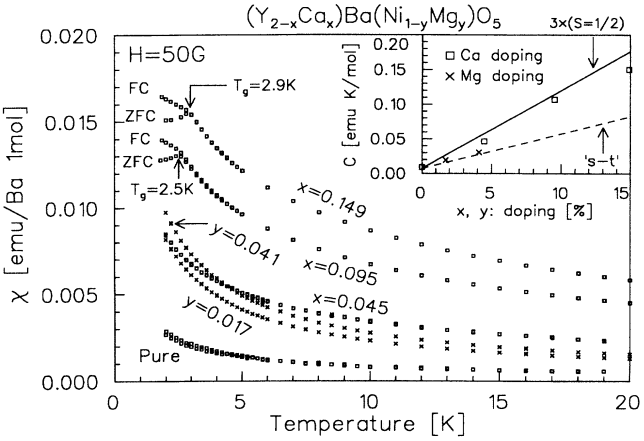

FIG. 1. Magnetic susceptibilities of $(Y_{2-x}Ca_x)Ba(Ni_{1-y}Mg_y)O_5$ ($x = y = 0$, $x = 4.5\%$, 9.5%, 14.9% and $y = 1.7\%$, 4.1%). The inset shows the doping dependence of the Curie constant. The solid line is from a model that one Ca creates three $s = 1/2$ spins. The broken line corresponds to the singlet-triplet model in Ref. [6].

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T_W). In the Ca doped samples, the Ca concentration (x) dependence of the Curie constant (C) suggests that one Ca^{2+} ion produces three $S = 1/2$ spins (solid line in the inset). These three $S = 1/2$ spins may be attributed to one Ni^{3+} ion (low spin state) and two $S = 1/2$ chain-end spins [11,12]. The Mg concentration (y) dependence of the Curie constant, on the other hand, is consistent with the heuristic "singlet-triplet" model [6]. In this model, *two* Mg^{2+} ions effectively create one $S = 1$ spin, giving the broken line shown in the inset. The Curie-Weiss behavior of the undoped Y_2BaNiO_5 has been interpreted as an effect of excess oxygen, which works as a hole dopant [9]. The Curie constant of our nominally pure specimen corresponds to the native chain breaks of 0.63(2) at. %. In the Ca doped systems ($x = 9.5\%$ and 14.9%), spin-glass behavior was observed with history dependent susceptibilities. The glass temperature (T_g) was determined to be 2.5 K (2.9 K) for the $x = 9.5\%$ (14.9%) system. The Mg doped systems, on the other hand, remain paramagnetic down to 2 K.

One possible reason for the different magnetic behaviors of the Ca and Mg doped systems is as follows: first, there is an effective interaction between the two chain-end spins in one broken chain [6]. The sign of this interaction depends on the length of the broken chain, giving randomness to the system. In the Ca doped system, there should be an additional Ni^{2+}-Ni^{3+}-Ni^{2+} superexchange coupling (J'), as is the case in an analogous system (Cu doped NENP) [12]. In the Mg doped system, on the other hand, there is no superexchange between the chain ends across a Mg^{2+} ion. Thus, the broken chains of the Mg doped system are isolated from each other, so that there is no chance for magnetic order, while the Ca doped system may freeze at $kT \lesssim J'$. It is very difficult to estimate the magnitude of J', but if one uses J' in Cu doped NENP ($\approx 0.7 \sim 0.9$ K), and assumes a scaling to the Haldane gap, J' in our system falls on the order of a few kelvin, which is consistent with T_g in the Ca doped systems.

We performed μSR measurements on $(Y_{2-x}Ca_x)Ba(Ni_{1-y}Mg_y)O_5$ systems at TRIUMF (Vancouver). Longitudinally polarized muons (spin $\parallel$ beam axis) were shot into the sintered polycrystalline pellets, which were placed on a 99.99% silver backing plate. We evaluated the time evolution of muon spins, using the conventional μSR technique [13].

In Fig. 2(a), we show time spectra of the muon spin polarization in the nominally pure ($x = y = 0$) system. The spectrum in zero field (ZF) shows a slow relaxation which does not disappear in an external longitudinal field (LF) of 100 G. This LF = 100 G measurement proves the dynamic nature of the muon spin relaxation: if the slow relaxation were due to a static random field distribution at the muon site, it would have been easily decoupled in a small LF $\sim$ 5 G [13]. In the pure system, we have confirmed the absence of static order down to 100 mK. The slow relaxation of the muon spin follows a square-root exponential function [$P_\mu(t) \approx \exp(-\sqrt{\lambda t})$], which is characteristic of dilute spin systems in a paramagnetic state [14]. Considering that our pure sample has native chain breaks of $\sim$0.6 at. %, it is likely that the muons detect local fields from chain-end spins. In Fig. 2(b), we compare μSR spectra from the pure, Ca doped ($x = 4.5\%$ and 9.5%) and Mg doped ($y = 4.1\%$) systems in the millikelvin regime. In the Ca 9.5% sample, there is fast muon spin relaxation, reflecting the spin-glass behavior. In the Mg 4.1% sample, muon spin relaxation is even *slower* than in the nominally pure system. This result suggests that the unpaired spins created by Mg doping have faster fluctuations than the native unpaired spins in the pure system.

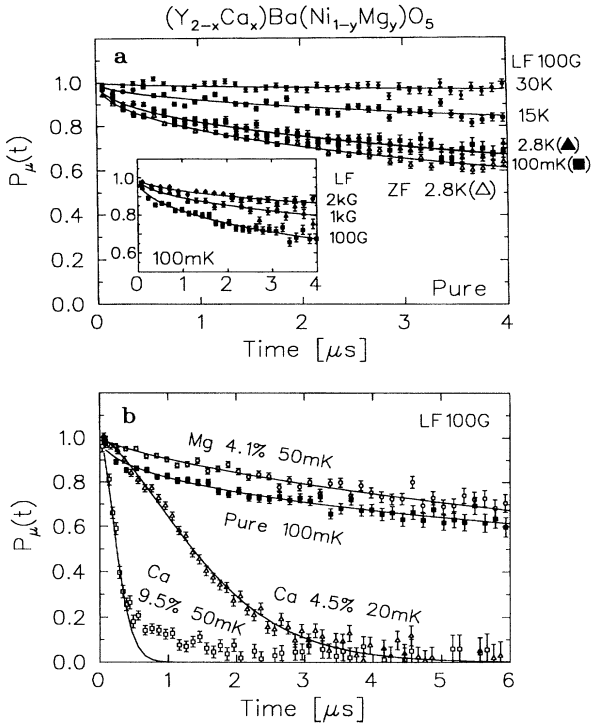

FIG. 2. (a) μSR spectra of the nominally pure Y_2BaNiO_5. The solid line is the fit with the square-root exponential function. (b) LF = 100 G μSR spectra are compared at $T \leq 100$ mK. The solid lines are the fit with the stretched exponential function.

We analyzed the μSR spectra with a phenomenological stretched-exponential function $\{\exp[-(\lambda t)^\beta]\}$. We were able to determine β and λ independently only for the Ca doped systems below 6 K. In this case, β approached 1.5 (Ca 4.5%) and 1.7 (Ca 9.5%) in the $T \to 0$ limit (not shown). In other systems, the relaxation was so slow that we had to freeze β to a temperature-independent value, in order to obtain the temperature dependence of λ. For the undoped system (all temperatures) and for the $T > 6$ K data of the Ca doped systems, we fixed $\beta = 0.5$, namely, to the square-root exponential function [14]. In the Mg doped systems, μSR spectra do not exhibit the fast front

end [Fig. 2(b)], suggesting that the β is larger than 0.5. We fixed β to 0.72 (Mg 1.7%) and 0.77 Mg 4.1%), which is the average of β, obtained by the preceding analysis without constraint on β. We show the relaxation rate (λ) in Fig. 3, as a function of temperature.

For the pure and Mg doped systems, λ at $T \lesssim 5$ K is temperature independent: this is a characteristic of paramagnetism. As shown in Fig. 4, we analyzed the LF dependence of λ using the T_1 relaxation theory for dilute spin systems [14], and obtained the field fluctuation rate (ν) and Lorentzian field width (a) at muon site. These two parameters are shown in Table I, as well as their estimations from the "dipolar-fluctuation model" [15]. In this model, the magnetic dipolar interaction is assumed to be the only interaction between the chain ends. The internal field at the muon position is also assumed to be the dipolar fields from the chain ends. We estimated the Lorentzian field width (a), using the method described in Ref. [14]. Since we do not know the muon site in this material, we assumed several possible muon sites, which are about 1 Å away from O^{2-} ions. In the framework of the "dipolar-fluctuation model," the ratio ν/a is on the order of the ratio of the electron and muon gyromagnetic factors ($\nu/a \approx 3/2\pi \times \gamma_e\gamma_\mu \approx 100$). The experimental result of the pure system follows this relation, while the Mg 1.7% doped system shows a slight enhancement of the fluctuation rate [$\nu/a = 600/2.0 = 300(50)$]. This enhancement may reflect the existence of additional coupling between the chain ends in vacancy doping [6], most likely due to the effective interaction through the chain [16].

In the pure system, λ decreases at $T \gtrsim 15$ K, indicating the existence of an additional thermally activated fluctuation process (Fig. 3). Since the decrease of λ was undetectable in the Mg doped system, this additional fluctuation in the pure system may be a spatial migration of the chain

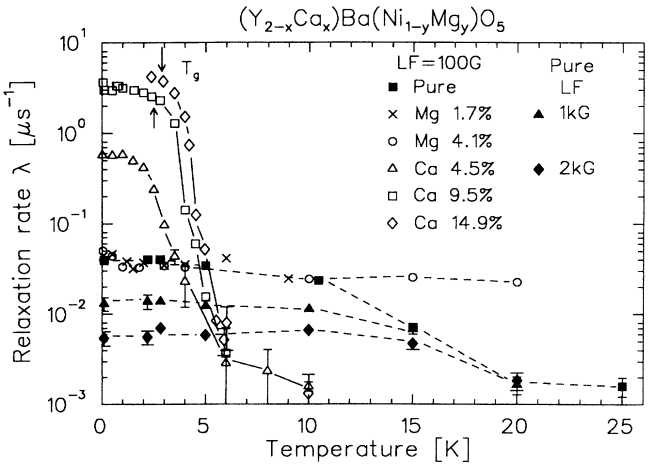

FIG. 3. Temperature dependence of muon spin relaxation rate (λ) measured in LF = 100 G. For the pure system, the results in LF = 1 and 2 kG are shown as well. The solid and broken lines are guides to the eyes.

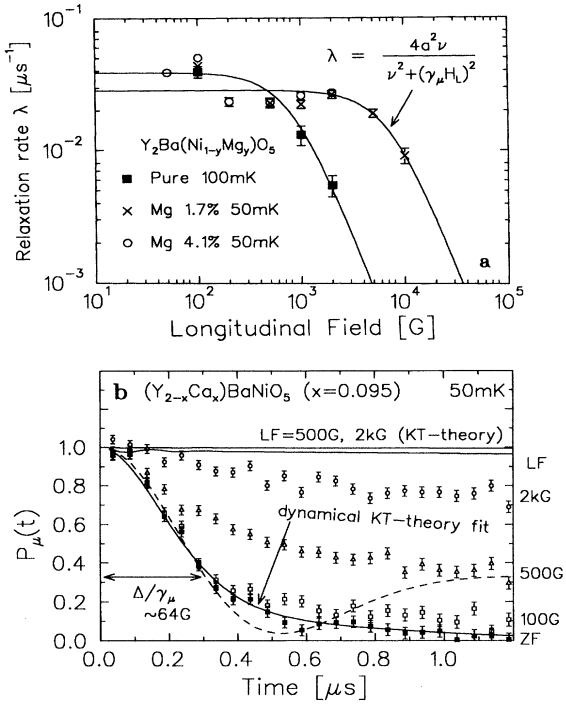

FIG. 4. (a) LF dependence of the muon spin relaxation rate (λ) at $T \leq 100$ mK. The solid lines are the fit with T_1 relaxation theory for dilute spin systems. (b) LF-μSR time spectra in the Ca 9.5% sample at 50 mK. The solid line on the ZF data is the fit with a dynamical Gaussian Kubo-Toyabe function. The broken line is the Kubo-Toyabe function in static case.

ends, which are generated by the residual charge from excess oxygen. In the Mg doped system, there is no chance of such migration, because the chain ends are pinned to the Mg site. In the Ca doped systems ($x = 9.5\%$ and 14.9%), Fig. 3 shows a sharp increase of λ with decreasing temperature toward T_g, reflecting the critical slowing down of the unpaired spins. In the Ca 4.5% sample, the temperature dependence of λ suggests a $T_g < 2$ K, which is beyond the temperature range of our SQUID magnetometer.

In Fig. 4(b), we show our μSR spectra at 50 mK in the Ca 9.5% system. The ZF spectrum behaves as a Gaussian in the early time range; this looks like the characteristic spectrum in a dense and almost static spin

TABLE I. The adjustable parameters in the T_1 relaxation fit.

Sample	Parameter	Experiment	Order estimation
Pure	a (μs^{-1})	0.74(4)	0.3–3[a]
	ν (MHz)	72(12)	30–300[b]
Mg 1.7%	a (μs^{-1})	2.0(2)	0.5–5[a]
	ν (MHz)	600(100)	50–500[b]

[a]Lorentzian width of the dipolar field distribution at muon site, generated by the chain breaks.
[b]Dipolar fluctuation rate of the chain-end spins.

system (Gaussian Kubo-Toyabe relaxation) [13]. In the framework of Kubo-Toyabe theory, the muon relaxation shows a recovery to 1/3, if the internal field is static [broken line in Fig. 4(b)]. The effect of slow dynamics is observed as a relaxation of this "1/3 component," until the fluctuation rate becomes fast enough ($\nu/\Delta \gtrsim 20$) to allow T_1 relaxation treatment. In this limit, the muon relaxation behaves as a single-exponential function. Thus, as long as the muon spin relaxation behaves as a Gaussian, the field fluctuation should be slow ($\nu \sim \Delta$) and the relaxation should be decoupled in a small LF comparable to Δ/γ_μ. But we have found that the Ca doped system does not follow this behavior: the LF dependence of the spectrum is much weaker than the dynamical Kubo-Toyabe theory suggests. If the Gaussian behavior in the ZF measurement were due to an almost static field distribution, the relaxation should have been decoupled in a LF $\sim$ 200 G, while in fact, the relaxation is present even at LF = 2 kG. The observed weak LF dependence of the muon spin relaxation clearly shows a dynamic nature of the local field even at $T/T_g = 0.02$.

Phenomenologically, the magnetic behavior of the hole doped Haldane system $[(Y_{2-x}Ca_x)BaNiO_5]$ is very similar to that of the Kagomé-lattice system ($SrCr_zGa_{12-z}O_{19}$), a geometrically frustrated antiferromagnet. In the $z = 8$ Kagomé system, susceptibility measurements have revealed an existence of a small portion of unpaired spins ($\sim$5% of the total chromium ions), which show a spin-glass-like cusp at $T_g \sim 3.5$ K. The ZF μSR spectrum in this system at $T \leq T_g$ approaches a Gaussian shape [17], while LF μSR measurements at 100 mK suggest very fast field fluctuations [4,17,18]. In the case of the Kagomé system, a model has been proposed to explain the origin of this "hardly-decoupled Gaussian" relaxation [17]. In that model, the persistent dynamics of the local field are attributed to the migration of a small number of the unpaired spins among an otherwise singlet-coupled majority. Considering that the doped charge cuts the spin chain in $(Y_{2-x}Ca_x)BaNiO_5$, it may be possible that the chain ends migrate like the unpaired spins in Kagomé-lattice systems. These persistent dynamics have never been observed in conventional spin-glass systems, and are possibly a common feature of "spin-liquid" ground state materials.

In conclusion, we have measured doped Haldane systems $(Y_{2-x}Ca_x)Ba(Ni_{1-y}Mg_y)O_5$ (nominally pure, x = 4.5%, 9.5%, 14.9% and y = 1.7%, 4.8%) with magnetic susceptibility and μSR. The nominally pure sample does not show any magnetic order down to 100 mK, supporting the singlet nature of the Haldane ground state. In the Mg doped systems, the unpaired spins generated by Mg doping remain paramagnetic down to T = 50 mK, while in the Ca doped systems (x = 4.5%, 9.5%, and 14.9%), spin-glass-like behavior was detected in the susceptibility. In contrast, μSR has revealed that the local field remains dynamic down to 50 mK. These persistent field fluctuations suggest that the ground state of the Ca doped systems may have some characteristics of a spin liquid.

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[1] F. D. M. Haldane, Phys. Lett. **93A**, 464 (1983); Phys. Rev. Lett. **50**, 1153 (1983).
[2] W. J. L. Buyers *et al.*, Phys. Rev. Lett. **56**, 371 (1986); J. P. Renard *et al.*, Europhys. Lett. **3**, 945 (1987); K. Katsumata *et al.*, Phys. Rev. Lett. **63**, 86 (1989).
[3] B. J. Sternlieb *et al.*, J. Magn. Magn. Mater. **104–107**, 801 (1992).
[4] Y. J. Uemura *et al.*, Hyperfine Interact. **85**, 133 (1994).
[5] D. J. Buttrey, J. D. Sullivan, and A. L. Rheingold, J. Solid. State Chem. **88**, 291 (1990).
[6] A. P. Ramirez, S-W. Cheong, and M. L. Kaplan, Phys. Rev. Lett. **72**, 3108 (1994).
[7] J. Darriet and L. P. Regnault, Solid State Commun. **86**, 409 (1993).
[8] B. Batlogg *et al.*, Physica (Amsterdam) **194–196B**, 173 (1994).
[9] N. Arikawa and K. Kiyono, thesis, University of Tokyo, 1993.
[10] J. F. DiTusa *et al.*, Phys. Rev. Lett. **73**, 1857 (1994).
[11] I. Affleck, T. Kennedy, E. H. Lieb, and H. Tasaki, Phys. Rev. Lett. **59**, 799 (1987); Commun. Math. Phys. **115**, 477 (1988).
[12] M. Hagiwara *et al.*, Phys. Rev. Lett. **65**, 3181 (1990).
[13] R. S. Hayano *et al.*, Phys. Rev. B **20**, 850 (1979).
[14] Y. J. Uemura *et al.*, Phys. Rev. B **31**, 546 (1985).
[15] K. Kojima *et al.*, J. Magn. Magn. Mater. **140–144**, 1657 (1995).
[16] T. Kennedy, J. Phys. Condens. Matter **2**, 5737 (1990).
[17] Y. J. Uemura *et al.*, Phys. Rev. Lett. **73**, 3306 (1994).
[18] A. Keren *et al.*, Hyperfine Interact. **85**, 181 (1994).