Magnetic Properties of the $S=2$ Heisenberg Antiferromagnetic Chain Compound MnCl$_3$(bpy)

M Hagiwara$^1$, Y Idutsu$^1$, Z Honda$^2$ and S Yamamoto$^3$

$^1$ KYOKUGEN (Center for Quantum Science and Technology under Extreme Conditions), Osaka University, Toyonaka, Osaka 560-8531, Japan

$^2$ Graduate School of Science and Engineering, Saitama University, Saitama 338-8570, Japan

$^3$ Department of Physics, Hokkaido University, Sapporo, Hokkaido 060-0810, Japan

E-mail: hagiwara@cqst.osaka-u.ac.jp

Abstract. We report the results of magnetic susceptibilities at temperatures between 2 and 300 K, and magnetization in magnetic fields of up to 52 T on polycrystalline samples of MnCl$_3$(bpy) (bpy=2,2′-bipyridine) and the comparison with numerical calculations. This compound is one of the rare examples of the spin 2 quasi-one-dimensional Heisenberg antiferromagnet, and the magnetic properties of tiny single crystal samples were reported previously. The temperature dependence of magnetic susceptibility and the magnetization curve after subtracting the contribution of magnetic impurity are well fitted to those calculated by a quantum Monte Carlo method with the intrachain exchange constant $J/k_B=31.2$ K and the $g$-value $g=2.02$ which are comparable to reported values ($J/k_B=34.8\pm1.6$ K and $g=2.04\pm0.04$).

1. Introduction
A large amount of experimental and theoretical studies have been performed since Haldane’s conjecture in 1983 [1] to elucidate the difference of the nature between Heisenberg antiferromagnetic chains (HACs) with half-integer and integer spin values. These efforts established the presence of the Haldane gap $\Delta$ in $S=1$ HAC systems, where $\Delta\sim0.41J$ and $J(>0)$ is the nearest-neighbor intrachain exchange constant. In particular, a Ni chain compound Ni(C$_2$H$_8$N$_2$)$_2$NO$_2$(ClO$_4$), abbreviated as NENP, has been investigated extensively by means of various experimental methods, because of the moderate gap energy due to the exchange constant $J/k_B$ of about 50 K and negligible interchain exchange interactions ($J'\sim10^{-4}J$).

On the other hand, there are few examples of the $S=2$ HAC systems which exhibit no long-range order at sufficiently low temperatures. This is probably caused by a very small energy gap ($\Delta\sim0.089J$) that was confirmed by several numerical calculations [2, 3]. In addition, the phase diagram of the $S=2$ HAC including single-ion ($D$) and exchange anisotropies was calculated [4] and it indicates the Haldane phase is maintained only for $D/J\leq0.04\pm0.02$. These theoretical findings might somehow depress experimental efforts to synthesize the $S=2$ HAC compounds in the Haldane phase.

In such a situation, the title compound MnCl$_3$(bpy), where bpy stands for 2,2′-bipyridine, was synthesized [5] and reported as the first evidence of the presence of the Haldane gap in an $S=2$ HAC [6]. Granroth et al. measured the temperature dependence of the magnetic susceptibility of tiny single crystals of this compound (2.4 mg), and found a broad peak near 100 K and a small anisotropy below 80 K. From the analysis of the magnetic susceptibilities, the intrachain
exchange constant $J$ and the $g$-value for the chain direction were evaluated ($J/k_B=34.8 \pm 1.6$ K and $g=2.04\pm0.04$). The fitting curve to the experimental susceptibility is unfortunately unclear in Ref. [6]. They also measured the magnetization curve of two single crystals of MnCl$_3$(bpy) at 30 mK and 1.4 K in magnetic fields of up to 16 T by utilizing a single crystal Si cantilever magnetometer, and determined a critical field, where the Haldane gap vanishes, for two directions parallel and perpendicular to the chains.

In the present paper, we compare the magnetic susceptibility after subtracting the contribution of paramagnetic impurities with that calculated by a quantum Monte Carlo method to clarify the intrinsic behavior of magnetic susceptibility in this compound. In addition, we extend the field region to 52 T to compare the magnetization curve with that calculated by the same method as in the fitting of the magnetic susceptibility.

2. Experimental and numerical calculation methods

Polycrystalline samples of MnCl$_3$(bpy), where bpy stands for 2,2′-bipyridine, were prepared according to the method A described in Ref. [5]. Mn$_{12}$O$_{12}$(CH$_3$CO)$_{16}$(H$_2$O)$_4$ [7], bpy and excess amount of (CH$_3$)$_3$SiCl were dissolved in CH$_3$CN. The solution was left to stand at 300 K for 24 h. The red-brown polycrystalline product was filtered and dried in air over night. The obtained compounds consist of Mn$^{3+}$ ions ($S=2$), but Mn$^{2+}$ ions must be contained as magnetic impurities because the compounds were synthesized by oxidizing an ingredient material with Mn$^{2+}$ ions. The temperature dependence of magnetic susceptibilities and magnetization at low fields of up to 7 T were measured with a commercial SQUID magnetometer (Quantum Design, MPMS-XL7). High field magnetization has been studied in pulsed magnetic fields of up to 52 T. The magnetization in pulsed magnetic fields was measured with an induction method using a pick-up coil, and the calibration was done using the low field data taken by the SQUID magnetometer. Both measurements were conducted at KYOKUGEN in Osaka University.

Magnetic susceptibilities and magnetization curves are calculated by a quantum Monte Carlo method for the $S = 2$ HAC. We define the spin Hamiltonian of the $S=2$ HAC as $\mathcal{H} = \sum_i JS_i \cdot S_{i+1} - \mu_B H \cdot \tilde{g} \cdot S_i$, where $S_i$ is the $S = 2$ quantum spin operator at the $i$th site, $\tilde{g}$ is the $g$-tensor of the spin, $\mu_B$ is the Bohr magneton and $H$ is the external magnetic field. We have calculated both open (97 spins) and unfrustrated periodic (96 spins) chains. Their thermodynamic properties are well convergent. The details of the calculations are described in Ref. [8].

3. Experimental results and discussion

The temperature dependence of magnetic susceptibility of a powder sample of MnCl$_3$(bpy) measured at 0.1 T is shown in Fig. 1. The raw data show an increase at low temperatures probably due to magnetic impurities. We assume the increase of magnetic susceptibility at low temperatures arising from Mn$^{2+}$ impurity ions coming from the ingredient mentioned above. The solid line indicates the paramagnetic contribution described by $xNg^2\mu_B^2S(S+1)/(3k_BT)$ with $g=2$, $S=5/2$, and $x=0.011$ where $N$ is the Avogadro number, and $k_B$ is the Boltzmann constant. Similar paramagnetic contribution can be calculated for $S=2$ (Mn$^{3+}$ ions) with $x=0.016$. The subtracted data with solid downward triangles have a round peak at about 100 K which is typical of low dimensional antiferromagnets.

Next, we compare the magnetic susceptibility with that calculated by a quantum Monte Carlo method for 96 spins with periodic boundary condition. Figure 2 indicates the results of the comparison. In the calculation, we use the parameter values of the $g$-value $g=2.02$ and the intrachain exchange constant $J/k_B=31.2$ K that are close to the reported values ($J/k_B=34.8\pm1.6$ K and $g=2.04\pm0.04$). The overall behavior of magnetic susceptibility is reproduced by the calculation except the anomaly at around 12 K.
The magnetization curve at low fields of up to 7 T in Fig. 3 shows a monotonous increase including the paramagnetic contribution derived from the magnetic susceptibility data. Therefore, we subtract the magnetization due to the paramagnetic contribution from the raw data. The broken line in Fig. 3 indicates the magnetization curve calculated with the Brillouin function for the impurity spin $S=5/2$ and the same concentration $x=0.011$ as used in the analysis of the magnetic susceptibility. The subtracted magnetization given by the solid line shows no magnetization up to about 1 T, indicating the existence of energy gap and the singlet ground state, and a linear increase above this field ($H_c$). This $H_c$ value is close to that determined for single crystal samples in Ref. [6].

Finally, we show in Fig. 4 high-field magnetization curve measured at 1.3 K in magnetic fields of up to 52 T. As well as the low-field magnetization data, the data contains the paramagnetic contribution, and thus we subtract the paramagnetic magnetization as above to get the intrinsic magnetization curve. The solid line in Fig. 4 is the intrinsic high-field magnetization curve. The open circles are calculated magnetization using the same parameters as in the magnetic susceptibility analysis. The agreement between experiment and calculation is satisfactory.

4. Conclusions
We have performed the magnetic susceptibility and magnetization measurements on polycrystalline samples of MnCl$_3$(bpy) and compared them with those calculated by a Monte Carlo method for 96 spins with periodic boundary condition. Both experimental results are...
Figure 3. Low field magnetization curve as a function of magnetic field of up to 7 T. The broken line indicates the magnetization curve calculated with the Brillouin function for the impurity spin $S=5/2$ and the concentration $x=0.011$.

Figure 4. High-field magnetization curve as a function of magnetic field of up to 52 T. The broken line indicates the raw magnetization curve, and the solid line shows the intrinsic magnetization curve after subtracting the magnetization due to magnetic impurities. Open circles are calculated magnetization using the same parameter values as in the magnetic susceptibility analysis.

satisfactorily fitted to the numerical results using the parameters of the $g$-value $g=2.02$ and the intrachain exchange constant $J/k_B=31.2$ K, which are close to the previously reported ones ($g=2.04\pm0.04$ and $J/k_B=34.8\pm1.6$ K). Since we used polycrystalline samples, it is difficult to evaluate the single ion anisotropy in this compound.

Acknowledgments
This work was partly supported by a Grant-in-Aid for Scientific Research B (No. 20340089) and the Global COE Program (Core Research and Engineering of Advanced Materials-Interdisciplinary Education Center for Materials Science)(No.10) from the MEXT, Japan.

5. References
[1] Haldane F D M 1983 Phys. Rev. Lett. 50 1153
[2] Todo S and Kato K 2001 Phys. Rev. Lett. 87 047203
[3] Nakano H and Terai A 2009 J. Phys. Soc. Jpn. 78 014003
[4] Schollwöck U and Jolicoeur T 1995 Europhys. Lett. 30 493
[5] Perlepes S P, Blackman A G, Huffman J C and Christou G 1991 Inorg. Chem. 30 1665
[6] Granroth G E, Meisel M W, Chaparala M, Jolicoeur Th, Ward B H and Talham D R 1996 Phys. Rev. Lett. 77 1616
[7] Lis T 1980 Acta Cryst. B36 2042
[8] Yamamoto S 1996 Phys. Rev. B 53 3364