Crystal Growth of a frustrated $J_1-J_2$ chain magnet
NaCuMoO$_4$(OH)

K Nawa$^{1,2}$, Y Okamoto$^{1,3}$, and Z Hiroi$^1$

$^1$ Institute for Solid State Physics, The University of Tokyo, Kashiwa, Chiba 277-8581, Japan
E-mail: knawa@tagen.tohoku.ac.jp

Abstract. In a frustrated $J_1-J_2$ chain magnet with ferromagnetic nearest neighbor interactions $J_1$ and antiferromagnetic next-nearest neighbor interactions $J_2$, novel quantum states such as a spin nematic state are theoretically expected to be present. To detect the novel states experimentally, it is required to find a suitable model compound and to obtain its sizeable and high-quality single crystals. Here we report synthesis of a single-crystalline NaCuMoO$_4$(OH), a model compound of frustrated $J_1-J_2$ chain magnet, by a hydrothermal method and discuss its magnetic properties. The temperature dependencies of magnetization are almost consistent with those of powder samples at high temperatures, while the peak in heat capacity divided by temperature associated with a magnetic transition becomes sharper and larger in the single crystal. This indicates the improved quality of the single-crystalline sample compared with the powder sample. Single-crystalline NaCuMoO$_4$(OH) should give a new experimental approach to the novel spin-nematic states expected near 26 T.

1. Introduction
One of interesting topics in solid state physics is to study an exotic state with an order parameter defined by a product of multiple spins [1–5]. A typical example is a spin nematic state with a order parameter $\langle s_i^+ s_{i+1}^- s_{j}^- s_{j+1}^+ \rangle$, where time-reversal symmetry is preserved but rotation symmetry is broken. Recently, a lot of theoretical studies have revealed that its long-range order can be lifted by competing interactions [1–5]. In this sense, a frustrated $J_1-J_2$ chain magnet, which contains competing ferromagnetic nearest-neighbor interactions $J_1$ and antiferromagnetic next-nearest-neighbor interactions $J_2$ in a magnetic field $B$

$$\mathcal{H} = J_1 \sum_l s_l \cdot s_{l+1} + J_2 \sum_l s_l \cdot s_{l+2} - g\mu_B B \sum_l s_l^z. \quad (1)$$

is interesting, because the spin nematic state is theoretically expected near the magnetic saturation [4–13]. However, its evidence has not been found experimentally because of some difficulties. First, detecting its subtle signatures is difficult; microscopic measurements such as NMR and neutron scattering experiments using sizeable single crystals are necessary [14–17]. Secondly, samples should have high-quality since the spin-nematic phase can be disturbed

$^2$ Present address: Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan

$^3$ Present address: Department of Applied Physics, Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan
or its weak signatures can be masked by disorder effects. For instance, the most studied compound LiCuVO$_4$ as a candidate system to realize the spin nematic state [18–26] includes small Li-deficiency, which induces a discrepancy between NMR and magnetization data below the magnetic saturation [26]. Thus, a new $J_1$-$J_2$ chain compound that overcomes these difficulties is required.

NaCuMoO$_4$(OH) is a new model compound of the frustrated $J_1$-$J_2$ chain magnet [27]. Exchange interactions are estimated to be $J_1 = -51$ K and $J_2 = 36$ K from magnetization and heat capacity measurements performed on a polycrystalline sample. The magnetic saturation field $B_s$ is 26 T, lower than $B_s = 41$ T for LiCuVO$_4$. The lower saturation field is advantageous for exploring the spin nematic phase by microscopic measurements in high fields. An apparent signature of a spin nematic state has not been detected in high-field magnetization measurements using polycrystalline sample [27]. However, further experiments using a single crystal would provide an evidence of the spin nematic phase, since smearing effects due to the magnetic anisotropy is removed. In this paper, we report a successful crystal growth of NaCuMoO$_4$(OH) and discuss their magnetic properties. A sharp and large peak due to a magnetic transition observed in heat capacity measurements indicates the improved sample quality of the single crystal.

2. Experiments

Single crystals were grown by the hydrothermal method. First, 8.0–28.0 mmol of MoO$_3$ was dissolved in 40 ml of an aqueous solution which includes 8.0–28.0 mmol of NaOH. Then 8.0–28.0 mmol of Cu(OH)$_2$ were added and the mixed solution was stirred for a while (10–120 minutes) in contact with cold water. The solution was put in a Teflon beaker of 100 ml volume, placed in a stainless steel autoclave, and heated at 160–240 °C for 7 days. The amount of starting materials, stirring time, and heating temperature were varied to find good conditions for crystal growth. The synthetic conditions are listed in table 1. After a heat treatment, rod-like crystals were picked up from black precipitation and washed by water. Obtained crystals were characterized by powder X-ray diffraction analysis using Cu $K\alpha$ radiation and single crystal X-ray diffraction analysis using Mo $K\alpha$ radiation (Rigaku, RINT-2000 and R-Axis RAPID, respectively). Magnetic susceptibility was measured in a SQUID magnetometer (Quantum Design MPMS), and heat capacity was measured by the relaxation method (PPMS, Quantum Design).

3. Results and discussion

The amount of starting material, stirring time before heating, and heating temperature were tuned appropriately to obtain a single crystal. Among several synthetic conditions listed in table 1, largest crystals were obtained when amount of starting materials, stirring time, and heating temperature were 18.2 mmol, 30 minutes, and 240 °C, respectively. Single crystals grew in the best condition is shown in Fig. 1(b). They are green in color but also include a dark-green or a black part. This is because they also include CuO and lindgrenite (Cu$_3$(MoO$_4$)$_2$(OH)$_2$ [28]) as inclusions. However, their amount is so small that we cannot detect them in a powder XRD pattern of powdered crystals.

When the total amount of starting materials was increased (decreased), the crystal became smaller and a lot of CuO (lindgrenite) crystals were produced after the reaction. Stirring time before heating was also crucial for the crystal growth. Figure 1 shows photographs of single crystals with different stirring time. Too short or long time of stirring makes the crystal small and increases the amount of inclusions. A surface state of Cu(OH)$_2$ particles might be important for the crystal growth.

To check the quality of the single crystal, we performed magnetization and heat capacity measurements. We discuss crystals synthesized in the best condition as judged (Fig. 1(b)) in
Figure 1. Photographs of single-crystalline NaCuMoO$_4$(OH) grown by hydrothermal method. The solution was stirred before the heat treatment for (a) 10 minutes, (b) 30 minutes, (c) 1 hours and (d) 2 hours. Yellow scale bars indicate 1 mm.

the following. Figure 2 shows temperature dependencies of magnetization divided by magnetic field, $M/H$. Its sample-dependence is little above 20 K but large below 20 K due to an additional contribution from lindgrenite, which exhibits ferrimagnetic order at $T_N = 14$ K [28]. A magnetic field of $B = 6.614$ T is applied to reduce its contribution. Red, green, and blue solid curves represent $M/H$ for $H \parallel a$, $b$, and $c$, respectively. Their temperature dependencies are quite similar to that of the powder sample represented by a black curve, indicating that magnetic anisotropy of NaCuMoO$_4$(OH) is small.

Table 1. Synthetic conditions of single-crystalline NaCuMoO$_4$(OH). The total amount of starting materials (NaOH, MoO$_3$, and Cu(OH)$_2$) with 40 ml of water, stirring time, and heating temperature, and a typical crystal size are listed. The optimized condition is emphasized by bold text.

| amount (mmol) | stirring time (min) | temperature (°C) | typical size (mm)          |
|---------------|--------------------|------------------|---------------------------|
| 8.0           | 30                 | 240              | –                         |
| 12.0          | 30                 | 240              | –                         |
| 16.0          | 30                 | 240              | 0.3×0.7×0.3               |
| 28.0          | 30                 | 240              | 0.2×0.5×0.2               |
| 18.2          | 10                 | 240              | 0.1×0.3×0.1 (Fig. 1(a))   |
| **18.2**      | **30**             | **240**          | **0.4×1.0×0.4 (Fig. 1(b))** |
| 18.2          | 60                 | 240              | 0.3×0.7×0.3 (Fig. 1(c))   |
| 18.2          | 120                | 240              | 0.2×0.5×0.2 (Fig. 1(d))   |
| 8.0           | 30                 | 160              | –                         |
| 18.2          | 30                 | 160              | –                         |
Figure 2. Temperature dependencies of magnetization divided by magnetic field, for $B \parallel a$, $b$, and $c$ in $B = 6.614$ T. Dashed curves stand for a simulated curve of the frustrated $J_1$--$J_2$ chain with $J_1 = -51$ K and $J_2 = 36$ K. Black solid curve indicates a temperature dependence of magnetic susceptibility of powder samples at 0.1 T.

The $M/H$ at 20--300 K is reproduced by the following function,

$$\frac{M}{H} = \frac{Ng_i^2\mu_B^2}{k_B J_2} \chi_{\text{chain}}(T) + \chi_0 \quad (i = a, b, c), \quad (2)$$

where $N$, $g_i$, $\chi_{\text{chain}}$, and $\chi_0$ indicate the Avogadro constant, diagonal components of $g$-tensor, magnetic susceptibility of frustrated $J_1$--$J_2$ chain, and temperature independent magnetic susceptibility, respectively. $\chi_{\text{chain}}$ is calculated for $J_1 = -1.4$ and $J_2 = 1$ by an exact diagonalization technique using ALPS package [29]. As shown in Fig. 2, experimental and simulated curves show good agreement. The best fit is obtained for $g_a = 2.15$, $g_b = 2.11$, $g_c = 2.35$, and $\chi_0 = 9.71 \times 10^{-5}$ cm$^3$ mol$^{-1}$. From the deviation of simulated curves below 15 K, the amount of lindgrenite is estimated to be less than 1 % in a molar quantity.

The improved quality of the single crystal is confirmed by heat capacity measurements. Figure 3 shows temperature dependencies of heat capacity divided by temperature, $C/T$, of a few single-crystalline and powder samples. A lattice contribution in $C/T$ is negligible and smaller than 0.2% of the total $C/T$ in this temperature range. Powder sample 2 is the same sample used in ref. [27], and powder sample 1 is a new sample prepared hydrothermally from 40 mmol of Na$_2$MoO$_4$·2H$_2$O, 1.912 mmol of Cu(NO$_3$)$_2$·3H$_2$O, and 10 ml of water. For all the samples $C/T$ exhibits a peak at about 0.6 K due to a magnetic transition. The peak apparently becomes sharp and large for the single-crystalline samples compared with the powder samples. Such a large difference in the peak magnitude indicates that small chemical disorder makes the magnetic transition diffusive, as is often the case with quasi-1D compounds. Single-crystalline sample 1 should have the best quality among the samples. The transition temperature $T_N$ is determined to be 0.63(1) K from the peak position, which is slightly higher than 0.59 K for the powder sample 2 [27]. The rough estimate of magnetic entropy $S_m$ below $T_N$ gives 0.17 J mol$^{-1}$, assuming that $C/T$ decreases to 0 by $T^3$ shown as a dashed curve in Fig. 3.

Now single-crystalline NaCuMoO$_4$(OH) with improved quality becomes available. It would enable further studies using a high magnetic field, such as magnetization and NMR experiments. We are now planning high field NMR experiments using a static magnetic field to elucidate the nature of the spin nematic phase. In addition, neutron scattering experiments are also possible
Figure 3. Temperature dependencies of heat capacity divided by temperature, $C/T$, in zero field. $C/T$ of two single-crystalline and two powder samples are compared. A dashed curve is assumed to estimate magnetic entropy $S_m$ of the single-crystalline sample 1.

by using a pulse field [30] or a static field [31, 32] owing to the saturation field of 26 T lower than that of LiCuVO$_4$. We believe that these experiments give a new insight for the novel spin-nematic state.

4. Summary
We succeeded in synthesizing single crystals of NaCuMoO$_4$(OH), a model compound of a frustrated $J_1$–$J_2$ chain magnet. The optimized condition for the crystal growth is reported. The magnetic transition of the single-crystalline samples is much sharper than that of powder samples, indicating their improved quality, while at high temperatures magnetic properties of both samples are almost consistent. Further experiments using single-crystalline NaCuMoO$_4$(OH) will uncover the physics of the $J_1$–$J_2$ chain magnet.

Acknowledgments
We thank H. Ishikawa, M. Yoshida, T. Masuda, S. Asai, and T. Oyama for fruitful discussions. This work was supported by Grant-in-Aid for Young Scientists (B) (No. 15K17693).

References
[1] Andreev A F and Grishchuk I A 1984 Zh. Eksp. Teor. Fiz. 87, 467–75.
[2] Shannon N, Momoi T, and Sindzingre P 2006 Phys. Rev. Lett. 96, 027213.
[3] Momoi T, Sindzingre P, and Shannon N 2006 Phys. Rev. Lett. 97 257204.
[4] Ueda H T and Momoi T 2013 Phys. Rev. B, 87, 144417.
[5] Zhitomirsky M E and Tsunetsugu H 2010 Europhys. Lett. 92, 37001.
[6] Chubukov A V 1991 Phys. Rev. B 44, 4693–96.
[7] Kecke L, Momoi T, and Furusaki A 2007 Phys. Rev. B 76 060407.
[8] Vekua T, Honecker A, Mikeska H -J, and Heidrich-Meisner F 2007 Phys. Rev. B 76, 174420.
[9] Hikihara T, Kecke L, Momoi T, and Furusaki A 2008 Phys. Rev. B 78, 144404.
[10] Sudan J, L’uscher A, and L’auclli A M 2009 Phys. Rev. B 80, 140402.
[11] Sato M, Hikihara T, and Momoi T 2013 Phys. Rev. Lett. 110, 077206.
[12] Starykh O A and Balents L 2014 Phys. Rev. B 89 104407.
[13] Balents L and Starykh O A 2016 Phys. Rev. Lett. 116 177201.
[14] Sato M, Momoi T, and Furusaki A 2009 Phys. Rev. B 79, 060406.
[15] Sato M, Hikihara T, and Momoi T 2011 Phys. Rev. B 83, 064405.
[16] Smerald A and Shannon N 2013 Preprint cond-mat/1303.4465v1; Smerald A and Shannon N 2016 Phys. Rev. B 93, 184419.
[17] Onishi H 2015 J. Phys. Soc. Jpn. 84, 083702.
[18] Lafontaine M A, Leblanc M, and Ferey G 1989 Inorg. Chem. C45, 1205–6.
[19] Enderle M, Mukherjee C, Fák B, Kremer R K, Broto J -M, Rosner H, Drechsler S -L , Richter J, Malek J, Prokofiev A, Assmus W, Pujol S, Raggazzoni J -L, Rakoto H, Rheinstädtler M and Ronnow H M 2005 Europhys. Lett. 70, 237–43.
[20] Böttgen N, Krug von Nidda H -A, Svistov L E, Prozorova L A, Prokofiev A, and Afms W 2007 Phys. Rev. B 76, 014440.
[21] Masuda T, Hagiwara M, Kondoh Y, Kaneko K, and Metoki N 2011 J. Phys. Soc. Jpn. 80, 113705.
[22] Mourigal M, Enderle M, Fák B, Kremer R K, Law J M, Schneidewind A, Hiess A, and Prokofiev A 2012 Phys. Rev. Lett. 109, 027203.
[23] Böttgen N, Kraetschmer W, Svistov L E, Prozorova L A, and Prokofiev A 2010 Phys. Rev. B 81, 052403.
[24] Nawa K, Takigawa M, Yoshida M, and Yoshimura K, 2013 J. Phys. Soc. Jpn. 82, 094709.
[25] Svistov L E, Fujita T, Yamaguchi H, Kimura S, Omura K, Prokofiev A, Smirnov A I, Honda Z, and Hagiwara M 2011 JETP Lett. 93, 21–5.
[26] Böttgen N, Nawa K, Fujita T, Hagiwara M, Kuhns P, Prokofiev A, Reyes A P, Svistov L E, Yoshimura K, and Takigawa M 2014 Phys. Rev. B 90, 134401.
[27] Nawa K, Okamoto Y, Matsuo A, Kindo K, Kitahara Y, Yoshida S, Ikeda S, Haras S, Sakurai T, Okubo S, Ohta H, and Hiroi Z 2014 J. Phys. Soc. Jpn. 83, 103702.
[28] Vilminot S, Andre G, Richard-Plouet M, Bourée-Vigneron F, and Kurmoo M 2006 Inorg. Chem. 45, 10938–46.
[29] Bauer B, Carr L D, Evertz H G, Feiguin A, Freire J, Fuchs S, Gamper L, Gukelberger J, Gull E, Gurtler S, Huhn A, Igarashi R, Isakov S V, Koop D, Ma P N, Mates P, Matsuo H, Parcollet O, Pollet L, Santos E, Scarola V W, Schollwöck U, Silva C, Surh B, Todo S, Trebst S, Troyer M, Wand M L, Werner P and Wessel S 2011 J. Stat. Mech. P05001; Albuquerque A F, Alet F, Corboz P, Dayal P, Feiguin A, Fuchs S, Gamper L, Gull E, Gurtler S, Honecker A, Igarashi R, Körner M, Koziukievich A, Läuchli A, Mannama S R, Matsumoto M, McCulloch I P, Michel F, Noack R M, Parcollet O, Pollet L, Pruschke T, Schollwöck U, Todo S, Trebst S, Troyer M, Werner P, Wessel S 2007 J. Mag. Mag. Mater. 310, 1187–93.
[30] Nojiri H, Yoshii S, Yasui M, Okada K, Matsuda M, Jung J -S, Kimura T, Santodonato L, Granroth G E, Ross K A, Carlo J P, and Gaulin B D 2011 Phys. Rev. Lett. 106 237202.
[31] Smeibidl P, Tennant A, Ehmler H, and Bird M 2010 J. Low Temp. Phys. 159, 402–5.
[32] Smeibidl P, Bird M, Ehmler H, Dixon I, Heinrich J, Hoffmann M, Kempfer S, Bole S, Toth J, Prokhnenko O, and Lake B, 2016 IEEE Trans. Appl. Supercond. 26, 4301606.