Powder neutron diffraction in one-dimensional frustrated chain compound NaCuMoO$_4$(OD)

S Asai[1], T Oyama[1], M Soda[1], K Rule[2], K Nawa[3], Z Hiroi[1], and T Masuda[1]

[1]Institute for Solid State Physics, The University of Tokyo, Kashiwanoha, Kashiwa, Chiba 277-8581, Japan

[2]Bragg Institute, Australian Nuclear Science and Technology Organization, Lucas Heights, New South Wales 2234, Australia

[3]Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Miyagi 980-8577, Japan

E-mail: `asai.shinichiro@issp.u-tokyo.ac.jp`

Abstract. We carried out powder neutron diffraction measurements in NaCuMoO$_4$(OD) in order to investigate the ground state of this material. We observe no temperature dependence between the powder neutron diffraction profiles at $T = 1.2$ and 0.07 K within the experimental error. We evaluate the maximum of the expected moment under the assumption that the helical magnetic order is realized and that the magnetic peaks are hidden in background scattering. We determined the positions of the D ions from the profile by using the Rietveld analysis.

1. Introduction

In $S = 1/2$ one-dimensional frustrated chain with nearest-neighbor ferromagnetic interaction J_1 and next-nearest-neighbor antiferromagnetic interaction J_2, the ground state exhibits various quantum phases depending on the ratio between J_1 and J_2 [1]. Theoretical study predicted that applying magnetic field induces exotic magnetic state, such as the spin multipole order in the vicinity of the saturation field [2]. However, such a state has not been well identified because of high saturation field and/or difficulty of obtaining a large crystal for the existing model compounds. For a famous model compound LiCuVO$_4$, the neutron scattering study suggests that the helical magnetic structure is the ground state in zero magnetic field [3]. The spin-flop transition [4] and the field-induced spin density wave state [5] were investigated by the neutron diffraction in the magnetic field. The magnetization-field curve indicated the presence of the unconventional magnetic state just below the saturation field of 44.4 T [6], but the field was too high to identify the spin correlation using neutron scattering technique.

Recently a new model compound NaCuMoO$_4$(OH) was reported [7]. The crystal structure [8] is shown in Fig. 1. Cu^{2+} ions carrying S = 1/2 form one-dimensional chain along the crystallographic b direction. The magnetic transition temperature of 0.6 K, the saturation field of 26 T, and the synthesis of a large single crystal were reported [7]. The field is covered by pulse magnet for neutron scattering [10] or hybrid magnet developed in Helmholz Zentrum Berlin [11]. Thus this compound is a good candidate for studying the quantum phases in the magnetic field. The ratio between J_1 and J_2 is evaluated to be -1.4 from the analysis
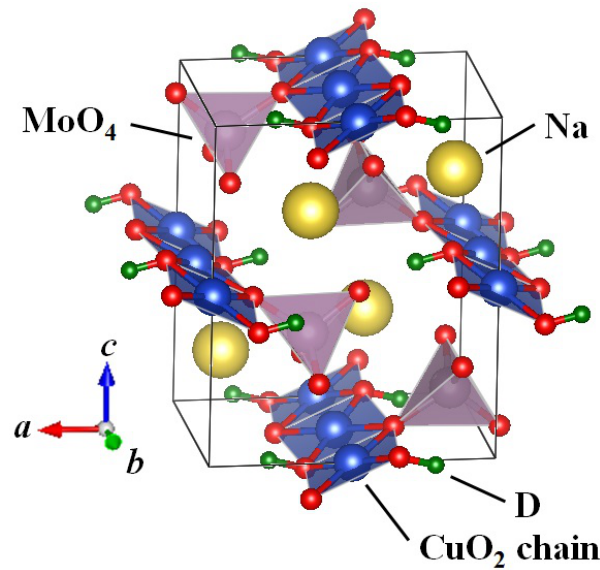
Figure 1. Crystal structure of $NaCuMoO_4(OD)$. The positions of the D ions are determined by this study. VESTA software [9] is used for drawing crystal structure.

of the magnetic susceptibility, which indicates that a helical magnetic order is realized at low temperature.

In this study, we performed neutron diffraction experiments in order to investigate the ground state of $NaCuMoO_4(OD)$, the D isotope for $NaCuMoO_4(OH)$. We observed no magnetic peak within the experimental error. We estimated the the moment size under the assumption that the helical magnetic order is realized and that the incommensurate magnetic peaks are hidden in background scattering. In addition we determined the position of the D ions from the diffraction profile by using the Rietveld analysis.

2. Experiments
The deuterated polycrystalline sample was synthesized by hydrothermal method. Neutron diffraction experiments were performed on thermal neutron triple-axis spectrometer TAIPAN at OPAL reactor, ANSTO [12]. The collimation setting was open - 40′ - 40′ - open. The PG filter was located in front of the analyzer. The incident neutron energy of 14.87 meV was used for the experiments. We used a dilution cryostat to achieve the temperature of 0.07 K. The deuterated isopropanol was put in the powder sample for improving the thermal conductivity of the sample. The obtained neutron patterns were analyzed by the Rietveld method using the FULLPROF software [13]. For simplicity, we fixed the occupancy parameters to be 1 and the isotropic temperature parameters to be 0 during the structure analysis.

3. Results and Discussions
Figure 2 shows the powder neutron diffraction pattens at $T = 0.07$ and 1.2 K. The magnetic peaks had been expected at $2\theta = 16.7$ and 24.2 deg. at 0.07 K in the case that the helical magnetic order was induced by the magnetic frustration with $J_1/J_2 = $ -1.4 [7]. We, howerver, did not observe any difference between the profiles and did not detect any magnetic peak. It is due to the high background intensity from incoherent scattering, which reduces the S/N ratio of the diffraction profile. We, then, presume that a magnetic signal is hidden in the background, and evaluate the maximum of the moment m, at best, by comparing an expected magnetic signal
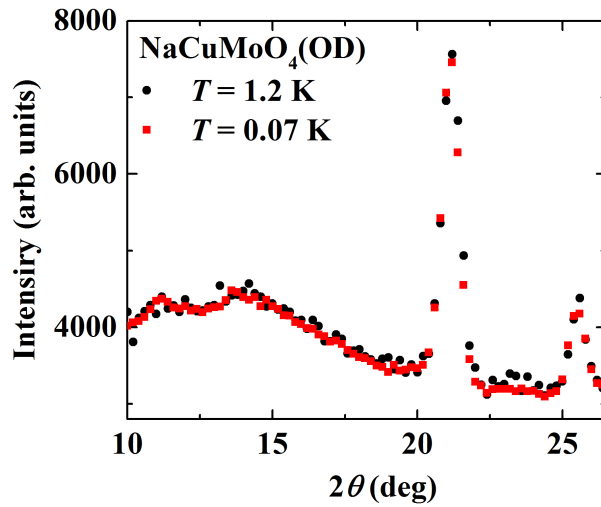
Figure 2. Powder neutron diffraction patterns at $T = 0.07$ and 1.2 K. Data are vertically scaled.
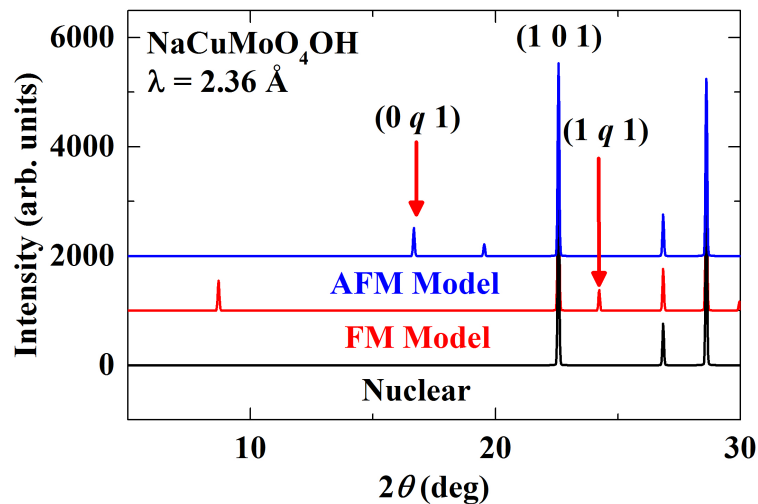

Figure 3. Calculated powder neutron diffraction patterns. The details of the AFM and FM models are shown in the main text.

with the statistical error of the background intensity. Here we assume that the spiral plane of the helical magnetic structure is in the crystallographic ab plane. We consider two cases; one is antiferromagnetically coupled chains, AFM model, and another is ferromagnetically coupled chains, FM model.

We first calculate the neutron diffraction profile in the case of $m = 1$ μ_{B} as shown in Fig. 3. In this paper, we does not consider the 2θ range below 10 deg. because this range is not covered by the TAIPAN spectrometer. The position, index number, and ratio of the intensity on the (101) nuclear peak for the largest magnetic peak are 16.4 deg., (0 q 1), and 0.149 for the AFM model, and 24.2 deg., (1 q 1), and 0.105 for the FM model in our calculation, where q is equal to 0.3862. Since the integrated intensity of the magnetic peak is proportional to m^2, the
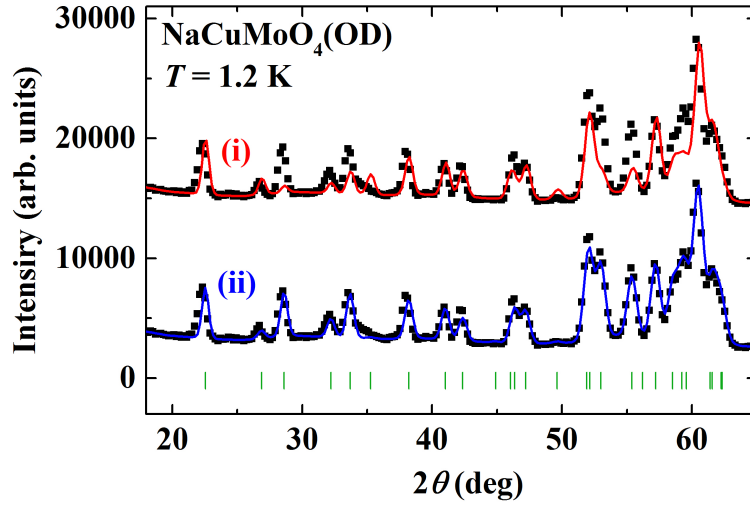
Figure 4. Powder neutron diffraction pattern at $T = 1.2$ K. The closed squares represent the experimentally obtained data. The upper and lower solid curves represent the calculated curves. The vertical bars below the closed squares represent the position of the nuclear Bragg peaks for NaCuMoO$_4$(OD).

intensities of the magnetic peaks are written as

$$I(0q1) = 0.149m^2 I(101) \tag{1}$$

and

$$I(1q1) = 0.105m^2 I(101) \tag{2}$$

for the AFM and FM models, respectively. Here $I(hkl)$ represents the intensity of the peak indexed as (hkl). We roughly evaluated $I(101)$ to be 10000 counts from the fitting the experimental data to the Gaussian function. The background intensities and their statistical errors at 16.7 and 24.2 deg. are about 12000 ± 109 and 10000 ± 100 counts, respectively. We substitute all of the evaluated value and derived equation shown above for the relation that the statistical error of the background intensity is larger than $I(0q1)$ and $I(1q1)$, and finally evaluated the ordered moment m to be below 0.27 and 0.31 μ_B for AFM and FM models, respectively. The neutron diffraction study by using the single crystal is needed for further investigation, which is now in progress.

Figure 4 shows the powder neutron diffraction pattens at $T = 1.2$ K. We can index all of the peaks by the orthorhombic structure with the space group $Pnma$ except for the aluminum one at 61 deg. The obtained lattice parameters are $a = 7.741(3)$, $b = 9.495(4)$, and $c = 5.960(2)$ Å. The solid curve (i) represents the calculated diffraction profile by using the structure model reported in Ref. 8. It does not reproduce the experimental data. We should note that the hydrogen ions were not taken into consideration in the previous structural analysis [8]. In fact, neutron diffraction profiles are much more affected by the presence of the hydrogen/deuteron ions than x-ray diffraction profiles are. Then we perform Rietveld analysis including the D ions. In order not to conflict with the chemical composition ratio, we assume that the D ions are located in special position denoted by $4a$, $4b$, or $4c$ in the crystal structure with the space group $Pnma$. We exclude the $4b$ Wyckoff position $(0, 0, 1/2)$ because Cu^{2+} ions occupy it. Firstly, we try the case that the D ions are in the $4a$ Wyckoff position $(0, 0, 0)$, but the calculated profile does not reproduce the data. Secondly we try the $4c$ Wyckoff position $(x, 1/2, z)$, and fit to the

data is reasonable as shown in the blue curve in Fig. 4. The position of the D ions is determined to be (0.243(4), 0.25, 0.030(4)) and is illustrated in Fig. 1.

4. Summary

We carried out powder neutron diffraction measurements for $NaCuMoO_4(OD)$ in order to investigate the ground state and crystal structure. We observed no temperature dependence between the profiles at $T = 1.2$ and 0.07 K within the experimental error. By comparing the expected magnetic signal with the statistical error, we evaluated the ordered moment to be less than 0.31 μ_B. In addition we determined the position of the D ions to be (0.243(4), 0.25, 0.030(4)).

References

[1] Furukawa S, Sato S M and, Onoda S 2010 *Phys. Rev. Lett.* **105** 257205.
[2] Hikihara T, Kecke L, Momoi T and Furusaki A 2008 *Phys. Rev. B* **78** 144404.
[3] Gibson B J, Kremer R K, Prokofiev A V, Assmus W, and McIntyre G J 2004 *Physica B* **350** e253.
[4] Yasui Y, Naito Y, Sato K, Moyoshi T, Sato M, and Kakurai K 2008 *J. Phys. Soc. Jpn.* **77** 023712.
[5] Masuda T, Hagihala M, Kondoh Y, Kaneko K, and Metoki N 2011 *J. Phys. Soc. Jpn.* **80** 113705.
[6] Svitov 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.
[7] Nawa K, Okamoto Y, Matsuo A, Kindo K, Kitahara Y, Yoshida S, Ikeda S, Hara S, Sakurai T, Okubo S, Ohta H, and Hiroi Z 2014 *J. Phys. Coc. Jpn.* **83** 103702.
[8] Moini A, Peascoe R, Rudolf P R, and Clearfield A 1986 *Inorg. Chem.* **25** 3782.
[9] Momma K and Izumi F 2011 *J. Appl. Crystallogr.* **44** 1272.
[10] 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.
[11] Prokhnenko O, Stein W -D, Bleif H -J, Fromme M, Bartkowiak M, and Wilpert T 2015 *Rev. Sci. Instr.* **86** 033102.
[12] Danilkin S A, Horton G, Moore R, Braoudakis G, and Hagen M E 2007 *J. Neutron Res.* **15** 55.
[13] Rodriguez-Carvajal J 1993 *Physica B* **192** 55.