Frustrated $S=3/2$ honeycomb antiferromagnet
$\text{Bi}_3\text{Mn}_4\text{O}_{12}(\text{NO}_3)$

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Abstract. Magnetic properties of a $S=3/2$ honeycomb antiferromagnet $\text{Bi}_3\text{Mn}_4\text{O}_{12}(\text{NO}_3)$ are discussed. Susceptibility and specific heat measurements showed
that this system is free from a long range ordering at least down to 0.4 K in a low
magnetic field because of the geometrical frustration caused by the competition
between the nearest and the next nearest interactions. On the other hand,
magnetization and neutron diffraction studies revealed a field-induced long range
ordering at around 10 K and 6 T.

1. Introduction
The magnetic properties of a solid reflect the arrangement of the magnetic ions in its crystal structure. Low-dimensional antiferromagnets exhibit a variety of ground states depending on the spin number and the spin configuration [1, 2]. The discovery of new $S=1/2$ kagome antiferromagnet without lattice distortion [3] and the confirmation of the absence of long-range ordering (LRO) in the $S=1/2$ triangle antiferromagnet NiGa$_2$S$_4$ [4] have drawn interest to the frustrated two-dimensional magnets. Honeycomb lattice can be regarded as a triangular derivative as well as Kagome lattice and is obtained by removing 1/3 of spins from a triangular lattice. Since an ideal antiferromagnetic (AF) honeycomb system with only the AF nearest-neighbor interaction ($J_1$) is free from frustration, the ground state is long-range ordering. However the system is frustrated if the next-nearest interaction ($J_2$) is also AF as shown in Fig. 3(b). According to theoretical calculations, honeycomb antiferromagnet does not show long range ordering when $J_2/J_1 > 1/6$ (for classical spin) or $> 0.15$ (for $S = 3/2$) [5,6].

Hydrothermal synthesis can produce crystal structures with cation environments and oxidation states unusual for high-temperature solid-state reaction conditions, and three new allotrophic forms of bismuth oxide were prepared under hydrothermal conditions [7–9] because this synthesis method stabilizes the distorted crystal structures due to the $6s^2$ lone pairs of Bi$^{3+}$ and the covalent Bi-O bonds. A further advantage of hydrothermal reaction is its ability to produce compounds otherwise unstable at high temperatures, such as those containing water or other gas species. Bismuth oxynitrates, such as $\text{BiMO}_4$(NO$_3$) ($M = \text{Sr, Ba}$), have flat NO$_3^-$ groups parallel to the $c$ axis but with bond angles different from 120° [11]. Since NO$_3^-$ groups separate the M-O networks in these compounds, bismuth oxynitrates with magnetic ions are expected to show two-dimensional magnetism. Planar and regular

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NO$_3^-$ groups with 120° O-N-O angles are also expected to act as a template for forming magnetic ions into triangular and triangle-derived lattices where magnetic frustration takes place [2]. In this paper we report the first example of bismuth-manganese oxynitrate Bi$_3$Mn$_4$O$_{12}$(NO$_3$) prepared by the hydrothermal method [10]. The edge-sharing MnO$_6$ octahedra form honeycomb lattices that are well separated by Bi and NO$_3^-$ layers. Despite the relatively large Weiss constant of $-252$ K, no long-range antiferromagnetic (AF) ordering was found at temperatures down to 0.4 K because of the magnetic frustration due to the presence of next-nearest AF interaction. More interestingly, a peculiar magnetic field induced long-range ordering was found by a neutron diffraction study.

2. Experimental
The sample powder was prepared from a mixture of Mn(NO$_3$)$_2$ · 6H$_2$O, NaBiO$_3$ by hydrothermal reaction at 543 K for 7 days in 70 mL Teflon-lined autoclaves. SEM pictures were taken using a JEOL JSM-6500F, and TEM and ED pictures were taken with a Topcon EM-002B. Neutron powder diffraction (NPD) measurement for structural determination was made, using a high-resolution powder diffractometer (HRPD) at the JRR-3 reactor of the JAEA site in Tokai, at a constant wavelength ($\lambda = 1.82307$ Å) in a vanadium container at room temperature. NPD in magnetic field was measured with triple-axis spectrometers TAS-2 with the fixed incident neutron energy of 14.7 meV and the energy resolutions ($\Delta E$) of 1.7 Magnetic susceptibility was measured with a SQUID magnetometer (Quantum Design MPMS XL) on heating after zero field cooling and on cooling in a magnetic field of 1000 Oe between 2 and 300 K by a relaxation method with a Quantum Design PPMS. The magnetization data were collected by extraction method with PPMS.

3. Results and Discussion
3.1. Structure refinement
The hydrothermal reaction yielded a fine black powder consisting of particles no more than about one micron across. A hexagonal platelet shape suggesting hexagonal or rhombohedral symmetry was observed by SEM as shown in Fig. 1 (a). Indexing of the electronic diffraction patterns provided the approximate dimensions of the hexagonal cell: $a \approx 5$ Å and $c \approx 13$ Å (Fig. 1 (b) and (c)). As no systematic absences were observed, the space group had to be chosen from 16 possible groups.

![Figure 1. SEM image of the powder obtained by hydrothermal reaction (a). Electron diffraction patterns of hexagonal Bi$_3$Mn$_4$O$_{12}$(NO$_3$) (b, c).](image)

When analyzing the x-ray diffraction data (not shown) with the lowest hexagonal symmetry group ($P6$), a combination of the direct method of structure solution from powder pattern implemented in EXPO2004 and the direct-space method implemented in FOX allowed us to locate heavy atoms in a structural model similar to PbSb$_2$O$_6$ (with bismuth in lead sites and with manganese in antimony sites) but having a $c$ parameter approximately three times longer. The hexagonal cell includes two PbSb$_2$O$_6$-like layers separated by a light-atoms layer unsolved from x-ray data. Since the presence of NO$_3^-$ groups in the structure was suggested by FT-IR measurements, similar to the signal seen in FT-IR spectroscopy results for YBi$_2$O$_4$NO$_3$ [12], the neutron diffraction data were analyzed on a model with NO$_3^-$ groups between the two PbSb$_2$O$_6$-like layers. Figure 2 shows the NPD pattern with the result of the Rietveld refinement. Further reduction of the space group to $P3$ was necessary to place the flat NO$_3^-$ group whose presence was indicated by the direct-space analysis of the neutron diffraction data.
The absence of inversion symmetry was verified by means of optical second harmonic generation measurement.

![Figure 2. Rietveld plot of neutron data for Bi₃Mn₄O₁₂(NO₃). Observed (circles), calculated (line) and difference (lower line) profiles are shown together with Bragg markers for the Bi₃Mn₄O₁₂(NO₃) phase and MnO₂.](image)

The refined crystal structure is illustrated in Fig. 3. The structural parameters refined from neutron data can be found elsewhere [11]. Since no sign of off-stoichiometry was observed, the occupancy factors were fixed to unity. The refinement showed the presence of 6.7 wt% MnO₂ as a secondary phase. To our knowledge, the novel bismuth manganese oxynitrate represents a new structural type. The bond valence sums calculated from the refined bond lengths listed in Table 1 indicate the following valence state: Bi³⁺Mn⁴⁺O⁻¹²(NO₃)⁻. The Mn⁴⁺ oxidation state is consistent with the formation of MnO₂ as the secondary phase. The manganese atoms have octahedral environment, slightly compressed along the c axis of the unit cell. The edge-sharing MnO₆ octahedra form honeycomb lattices as schematically illustrated in the inset of Fig. 3(b). The bismuth atoms, on the other hand, are in distorted environments. Bi1 is also in an octahedron but is shifted from the center. Bi2 and Bi3 have umbrella-like coordinations. They have three short Bi2(3)-O2(3) bonds on one side and six long Bi2(3)-O5(5) bonds on the other side. These environmental distortions might be explained by the space needed for the lone pairs of Bi³⁺. The distance between PbSb₂O₆-like layers and NO₃ layers is quite large: the Bi2-O5 distance is 3.1 Å and the Bi3-O5 distance is 3.2 Å. Since each of these distances is significantly greater than the sum of the ionic radii, the bonding should be rather weak.
### Figure 3. Refined crystal structure of Bi$_3$Mn$_4$O$_{12}$(NO$_3$) (a) and antiferromagnetic pathways in a honeycomb layer (b).

### Table 1. Selected bond distances

| Bond                  | r (Å)  | Bond                  | r (Å)  |
|-----------------------|--------|-----------------------|--------|
| Bi(1) – O(1) (× 3)    | 2.29(5)| Mn(1) – O(1) (× 3)    | 1.82(5)|
| – O(4) (× 3)          | 2.41(6)| Mn(2) – O(1) (× 3)    | 1.80(6)|
| Bi(2) – O(2) (× 3)    | 2.18(5)| O(2) (× 3)           | 2.00(6)|
| – O(5) (× 3)          | 3.06(5)| O(2) (× 3)           | 1.97(6)|
| – O(5) (× 3)          | 3.08(5)| Mn(3) – O(3) (× 3)   | 1.89(5)|
| Bi(3) – O(3) (× 3)    | 2.12(5)| O(4) (× 3)           | 1.86(5)|
| – O(5) (× 3)          | 3.22(6)| Mn(4) – O(3) (× 3)   | 1.86(5)|
| – O(5) (× 3)          | 3.23(6)| O(4) (× 3)           | 1.89(6)|
| N – O(5) (× 3)        | 1.23(4)| Mn(1) – O(1) (× 3)   | 1.82(5)|

### 3.2. Magnetic measurements in a low field

Because the Bi$_3$Mn$_4$O$_{12}$(NO$_3$) pellet solidified at 6 GPa was highly resistive, the system can be regarded as a localized spin system. The temperature dependence of the magnetic susceptibility on a sample free from MnO$_2$ shown in Fig. 4(a) shows a broad maximum centered at about 70 K. This broad maximum is a characteristic feature of a low-dimensional antiferromagnet and is consistent with the two-dimensional crystal structure. Fitting the data between 300 and 400 K to the Curie-Weiss law $\chi = C/(T-\theta) + \chi_0$ where $C$ is the Curie constant, $\theta$ is the Weiss constant, and $\chi_0$ is the temperature-independent term gave $C = 2.07, \theta = -252$ K, and $\chi_0 = -8.73 \times 10^{-4}$ emu/mol. This relatively large negative $\chi_0$ should be attributed to the presence of heavy element, Bi. The Curie constant is as expected for a Mn$^{4+}$ ($S = 3/2$) system and is thus consistent with the 4+ oxidation state determined for Mn in the structure analysis. Despite the large AF Weiss constant, no sign of LRO was observed. The deviation of ZFC and FC data are not an indication of the LRO because no corresponding anomaly is evident in the specific heat data (Fig. 4(b)). It should be attributed to the spin glass freezing as
confirmed by μSR measurement [13]. Figure 4(b) shows the temperature dependence of the specific heat divided by the temperature (\(C_p/T\)). Since there is no nonmagnetic reference, the lattice contribution is not subtracted. The \(C_p/T\) data show a broad maximum at around 40 K and decrease to zero with decreasing temperature. No other peak is found between 0.4 and 300 K, confirming the absence of the LRO.

Figure 4. (a) Temperature dependence of the magnetic susceptibility of Bi₃Mn₄O₁₂(NO₃) in zero field cooling and field cooling conditions. Inset shows the magnified view between 2K and 12 K. (b) Total specific heat divided by temperature of Bi₃Mn₄O₁₂(NO₃) solidified pellet.

Bi₃Mn₄O₁₂(NO₃) showed a two-dimensional magnetism consistent with the determined crystal structure. Because of its threefold symmetry, the honeycomb lattice of Mn⁴⁺ (\(S = 3/2\)) is uniform, without any distortion. It should also be pointed out that the orbital ordering as proposed for a \(S = 1/2\) Kagome compound Cu₃V₄O₉(OH)₂·2H₂O [14] doesn’t take place in this compound because of the \(d^9\) nature of Mn⁴⁺ ion. Despite the AF Weiss temperature of \(-252\) K, no LRO was observed down to 0.4 K. The ground state of an ideal AF honeycomb lattice system with only the AF nearest-neighbor interaction is LRO because the system is free from frustration. If next-nearest interaction is also AF, however, the system is frustrated [5,6]. In the present compound the nearest AF interaction mediated by the orthogonal Mn-O-Mn bond is rather weak. Considering the Weiss temperature of \(-252\) K and the number of the nearest-neighbor spins, 3, one would expect the exchange interaction to be smaller than 100 K. The next-nearest interaction mediated by the Mn-O-O-Mn bond is therefore not negligible. The current compound is the first example of frustrated honeycomb antiferromagnet without long-range ordering. The ground states of such systems with classical [5] and quantum [6] spins had been investigated theoretically, but no actual compound had been known. It was predicted that the \(S = 3/2\) honeycomb system with \(J_2 / J_1 > 0.16\) would not exhibit a long-range ordering [6]. Further quantitative analyses of the susceptibility and specific heat data are desirable.

3.3. High-magnetic field behaviour
Although Bi₃Mn₄O₁₂(NO₃) has no long-range ordering, magnetization shows a small jump of \(-0.1\mu_B/f.u.\) around 6-13 T below 20 K, as shown in Fig. 5(a), indicating a transition to a metamagnetic phase. In order to clarify the nature of the magnetic field-induced phase, we performed neutron scattering experiments under applied magnetic fields [15].
Figure 5. (a) Magnetization versus magnetic field in dc (T <10 K) and pulsed fields (T >15 K) for Bi$_3$Mn$_4$O$_{12}$(NO$_3$) in a temperature range between 2 and 200 K. (b) Temperature-magnetic field phase diagram. LRO and SRO stand for the long-range and short-range ordered phases, respectively. (c) Total specific heat divided by temperature measured in 0 and 9 T.

Figure 6. (a) Neutron powder diffraction patterns in Bi$_3$Mn$_4$O$_{12}$(NO$_3$) with $\Delta E \sim$1.7 meV at $H$=0 and 10 T and at $T$=3 K. At 10 T the broad magnetic peak is reduced and sharp magnetic peaks appear. The magnetic field (b) and temperature dependences (c) of the elastic magnetic signal at $Q$=1.60 and 1.74 Å$^{-1}$. The signals at 1.60 and 1.74 Å$^{-1}$ mostly originate from the short-range order and the 3D long-range order, respectively. In all the data shown here, the background signal was subtracted.

Figure 6(a) shows the neutron powder diffraction patterns in Bi$_3$Mn$_4$O$_{12}$(NO$_3$) at $H$=0 and 10 T. The spectrum at 0 T shows a broad peak originating from the short-range antiferromagnetic order as suggested by susceptibility and specific heat measurements. With application of magnetic field at $T$=3 K, the broad magnetic intensity is reduced and resolution-limited sharp magnetic Bragg peaks appear above $H \sim$6T, as shown in Fig. 6(b). This result indicates that long-range magnetic order is induced in magnetic field. Figure 6(c) shows the temperature dependence of the elastic magnetic signals at $Q$=1.60 and 1.74 Å$^{-1}$ at $H$=10 T. The signal originating from the long-range order vanishes and that from the short-range order recovers around 18 K. Since the most intense peak is the (1, 0, 1) reflection, the nearest-neighbor spins align antiparallel both in the $ab$ plane and along the $c$ axis. Therefore, there is no frustration in the magnetic structure. Since the width of the magnetic field-induced sharp peak is almost the same as the instrumental resolution, it is evident that the magnetic structure is long-ranged and commensurate. From the results of the magnetic structural analysis, we determined that the spins lie in the $ab$ plane and that the ordered moment is $\sim$1.8 $\mu_B$ at 3 K. The moment size is about 2/3 of the
full moment $3 \mu_B$ for the Mn$^{4+}$ ion. As shown in Fig. 6(a), there still exists a broad signal around 1.6 Å$^{-1}$ at 10 T. This is the remnant of the broad peak observed in the zero magnetic field. This suggests that the field-induced transition depend on magnetic field direction and that only the magnetic moments perpendicular to the magnetic field contribute to the ordering and the others remain disordered. It is puzzling why the transition depends on the field direction, although the compound is an isotropic Heisenberg system. The magnetic field-temperature phase diagram is summarized in Fig. 5(b). We observed the magnetic field-induced phase transition, in which the short-range order expands into the long-range Néel order by applying magnetic field. This indicates that this compound is located near the boundary of the ordered and disordered phases with $J_2/J_1$ close to 0.15. Accordingly the specific heat measured in a magnetic field of 9T shown in Fig. 5 (c) doesn’t show any peak. The entropy change at the ordering is undetectably small. The transition temperature increases with increasing magnetic field in this compound as shown in Fig. 5(b). This indicates that the collinear Néel state becomes more stabilized at higher temperatures. This may suggest that thermal fluctuations stabilize the Néel order, where “order by disorder” mechanism is at work [16].

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