Two Magnetic Orderings and a Spin–Flop Transition in Mixed Valence Compound Mn$_3$O(SeO$_3$)$_3$

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Abstract: A mixed-valence manganese selenite, Mn$_3$O(SeO$_3$)$_3$, was successfully synthesized using a conventional hydrothermal method. The three-dimensional framework of this compound is composed of an MnO$_6$ octahedra and an SeO$_3$ trigonal pyramid. The magnetic topological arrangement of manganese ions shows a three-dimensional framework formed by the intersection of octa-kagomé spin sublattices and staircase-kagomé spin sublattices. Susceptibility, magnetization and heat capacity measurements confirm that Mn$_3$O(SeO$_3$)$_3$ exhibits two successive long-range antiferromagnetic orderings with $T_{N1} \approx$4.5 K and $T_{N2} \approx$45 K and a field-induced spin–flop transition at a critical field of 4.5 T at low temperature.

Keywords: mixed-valence; magnetic properties; topological structures

1. Introduction

Mixed valence transition metal (TM) oxides with three-dimensional electronic configurations are of great significance in the fields of materials chemistry, electrochemical energy and condensed matter physics due to their diverse crystal structures and electronic configurations [1,2]. From the ancient application of Fe$_3$O$_4$ in the compass to today’s copper-based high temperature superconducting materials, mixed valence TM oxides exhibit exciting and unusual chemical and physical behaviors, including high-temperature superconductors [3], colossal magnetoresistance [4], ion deintercalation [5], metal-insulator transition [6], electrocatalysis/photocatalysis [7,8], etc. More specifically, copper oxides with bidimensional characters, together with the mixed valency of Cu$^+$/Cu$^{2+}$ or Cu$^{2+}$/Cu$^{3+}$, are responsible for superconducting properties [9,10]. The ferromagnetic (FM) material La$_{0.67}$Sr$_{0.33}$MnO$_3$ exhibits metallic conductivity due to the Zener double exchange mechanism between Mn$^{3+}$ and Mn$^{4+}$ ions, but BaFe$_{12}$O$_{19}$ (also an FM material) is insulative due to the limitation of the ratio of Fe$^{2+}$ and Fe$^{3+}$ ions [11]. Compound K$_2$Cr$_3$O$_6$ (hollandite), with a rare Cr$^{3+}$/Cr$^{4+}$ mixed valence state, exhibits a metal-insulator transition in a FM state [12]. The transition metal valence state of cathode material LiMO$_2$ (M = Mn, Co, Ni) will switch back and forth between M$^{2+}$ and M$^{4+}$ during charging and discharging processes in Li-ion batteries [13,14].

X. Yu et al. reported the experimental observation of skyrmionic bubbles with various topological lattices in colossal magnetoresistive manganite La$_{1-x}$Sr$_x$MnO$_3$ [15]. In order to discover new materials with unusual physical/chemical properties, it is necessary to explore new mixed-valence transition metal compounds. The compound Mn$_3$O(SeO$_3$)$_3$ (Mn$^{2+}$Mn$^{3+}$O(SeO$_3$)$_3$) was first reported by Wildner [16]. Structure analysis confirmed that this compound shows a channel structure with a three-dimensional magnetic topological framework formed by the intersection of octa-kagomé spin sublattices and staircase-kagomé spin sublattices; however, there are few studies regarding its magnetic properties. In this paper, we report the discovery of a mixed valence manganese selenate Mn$_3$O(SeO$_3$)$_3$. 

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Magnetic measurements indicate that this compound possesses two successive antiferromagnetic (AFM) transitions at low-temperature. Moreover, a spin-flop transition is observed at 2 K with an applied magnetic field of ~4.5 T.

2. Experimental Section

2.1. Synthesis of Mn$_3$O(SeO$_3$)$_3$

Single crystals of Mn$_3$O(SeO$_3$)$_3$ were obtained using a conventional hydrothermal method. A mixture of 2 mmol Mn(NO$_3$)$_2$·xH$_2$O (3 N, 0.3943 g), 2 mmol LiI (2 N, 0.2704 g), 1 mmol SeO$_2$ (4 N, 0.1110 g) and 5 mL deionized water was sealed in an autoclave equipped with a Teflon liner (28 mL). The autoclave was gradually heated to 230 °C at a rate of 1 °C/min, held for 4 days and then naturally cooled to room temperature. The product contained the desired black noodle-like crystals with a 90% yield. The crystals’ sizes and morphologies were characterized using a stereomicroscope and field emission scanning electron microscopy (FE-SEM, SU8100, Hitachi, Tokyo, Japan). Figure S1 shows images of the crystals under the stereomicroscope and FE-SEM. It can be observed that the crystal size is approximately 0.3 × 0.08 × 0.05 mm. The product’s impurities were manually removed under a microscope. Powdered samples were prepared for physical measurement by crushing small single crystals; purity was confirmed by powder X-ray diffraction (XRD) analysis (Figure 1). Moreover, the reagent LiI acted as a mineralizer, as the quality of crystals was unsatisfactory without it.

Figure 1. Rietveld refinement of powder X-ray (Cu Kα) diffraction patterns for Mn$_3$O(SeO$_3$)$_3$. The refined lattice constants are $a = 15.484(9)$ Å, $b = 6.665(8)$ Å, $c = 9.703(1)$ Å and $β = 118.79(4)^\circ$ with space group C2/m, which is consistent with the reported parameters of ref. [16].

2.2. Methods

XRD patterns were collected using a Bruker D8 diffractometer with Cu-Kα radiation ($λ$=1.5418 Å) at room temperature. Rietveld refinement was performed using GSAS-EXPGUI software [17]. Refined crystal structures were analyzed using VESTA software [18]. Furthermore, element analysis was observed using FE-SEM with an X-ray energy-dispersive spectrometer (EDS). EDS analysis confirmed the molar ratio of Mn/Se as 3.1/2.0, which is in good agreement with the X-ray structure analysis. Thermogravimetric
analysis (TGA) of Mn$_3$O(SeO$_3$)$_3$ was collected on NETZSCH STA 449C instruments with an Al$_2$O$_3$ crucible from 50 to 900 °C at a rate of 10 °C/min under N$_2$ atmosphere.

Magnetic measurements of a powdered sample of Mn$_3$O(SeO$_3$)$_3$ were performed using a PPMS (Quantum Design, San Diego, CA, USA). The powdered sample (20.6 mg) was placed in a plastic capsule, which was suspended in a copper tube slot. Magnetic susceptibility was measured at 0.1 T from 2 to 300 K. Magnetization was measured at different temperatures at applied field from 0 to 9 T. Heat capacity was measured with the same PPMS system at zero field and determined using a relaxation method on a 5.6 mg sample.

3. Results and Discussion

The structure of compound Mn$_3$O(SeO$_3$)$_3$ was first reported by Wildner [16]. Mn$_3$O(SeO$_3$)$_3$ crystallizes in the monoclinic system with the space group $C2/m$. As shown in Figure S2, both Mn and Se atoms have three crystallographic sites. The oxidation state is +2 for Mn$^{2+}$ and +3 for Mn$^{3+}$. All manganese atoms are coordinated by six oxygen atoms forming MnO$_6$ distorted octahedra; Mn–O bond lengths range from 2.100(1) to 2.361(8) Å for Mn$^{2+}$O$_6$ octahedra and from 1.854(2) to 2.310(6) Å for Mn$^{3+}$O$_6$ and Mn$^{3+}$O$_6$, respectively. In other words, the degree of distortion for Mn$^{2+}$O$_6$ octahedra is smaller than that of Mn$^{3+}$O$_6$ and Mn$^{3+}$O$_6$. This is due to the Mn$^{3+}$ $(t^2_g, 3e_g, 1e_g)$ octahedron with a remarkable Jahn–Teller effect, which may induce a larger structure distortion than Mn$^{2+}$ $(t^2_g, 3e_g, 2e_g)$. All selenium atoms are in trigonal pyramid geometry with a stereoactive lone pair of 4 s$^2$ in Se$^{4+}$ ions; the Se–O bond lengths are approximately 1.70 Å. It should be noted that Se1/Se2/Se3 atoms are surrounded by 4/5/6 manganese atoms with a Se–O–Mn route, respectively. These 4/5/6 manganese atoms contain two Mn$^{2+}$ atoms and 2/3/4 Mn$^{3+}$ atoms, respectively.

As shown in Figure 2, Mn$_3$O(SeO$_3$)$_3$ shows a tunnel structure along the b-axis, in which the framework is constituted by MnO$_6$ octahedra and SeO$_3$ trigonal pyramids. Mn$^{3+}$O$_6$ octahedra share their edges (O5–O6) to form uniform -[Mn$_1$-] chains along the b-axis. Mn$^{3+}$O$_6$ octahedra are interconnected via edge-sharing oxygen atoms, forming a two-dimensional -[Mn$_{3+}$] layered structure parallel to (001). The detailed linkage mode between manganese ions is shown in Figure 3. Two Mn$^{2+}$O$_6$ octahedra connect to each other by edge-sharing oxygen atoms (O4–O4) to form a [Mn$_{2}O_{10}$] dimer along the a-axis. The Mn2-O4-Mn2 angle is 101.34(9)$^\circ$. Mn$^{3+}$O$_6$ octahedra are interconnected by corner-sharing oxygen atoms (O7) to form uniform -[Mn$_{3+}$] chains along the b-axis. One Mn$^{2+}$O$_6$ octahedron and two Mn$^{3+}$O$_6$ octahedra are connected in an isosceles triangle configuration. The neighbored -[Mn$_{3+}$] layers are separated by -[Mn$^{2+}$] chains and SeO$_3$ trigonal pyramids. Furthermore, we noted that Mn$^{3+}$O$_6$ octahedra are interconnected with Mn$^{2+}$O$_6$ octahedra via corner-sharing O5 atoms, but Mn$^{3+}$O$_6$ and Mn$^{3+}$O$_6$ octahedra are connected by SeO$_3$ groups in the manner of Mn$^{1+}$O–Se–O–Mn3. After removing the nonmagnetic SeO$_3^{2−}$ groups, the topological arrangement of magnetic Mn ions is a three-dimensional framework (Figure 2b). Mn$^{3+}$ ions form a two-dimensional octa-kagomé lattice parallel to (001) (Figure 2c). The adjacent octa-kagomé layers are connected by -[Mn$^{1+}$-] chains. It is significant that there is a staircase-kagomé lattice composed of Mn$^{2+}$ and Mn$^{3+}$ parallel to (100) in the magnetic topological framework (Figure 2d). The shortest Mn–Mn distance in both -[Mn$^{1+}$-] and -[Mn$^{3+}$-] chains is 3.332(9) Å. However, the detailed connection mode of Mn$^{2+}$O$_6$ octahedra in -[Mn$^{1+}$-] chains are edge-sharing, whereas in -[Mn$^{3+}$] chains it is corner-sharing. The Mn–O–Mn angles in -[Mn$^{1+}$-] and -[Mn$^{3+}$-] chains are 89.77(1)$^\circ$ / 102.90(8)$^\circ$ and 127.61(5)$^\circ$, respectively. The Mn$^{2–}$Mn2 and Mn$^{2–}$Mn3 distances in the octa-kagomé lattice are 3.150(0) Å and 3.069(6) Å, respectively, whereas the Mn$^{1+}$Mn2 distance is 3.902(1) Å.
The octahedra in [-Mn1-] chains are edge-sharing, whereas in [-Mn3-] chains it is corner-sharing. The Mn-O-Mn angles in [-Mn1-] and [-Mn3-] chains are 89.77(1)°/102.90(8)° and 127.61(5)°, respectively. The Mn2--Mn2 and Mn2–Mn3 distances in the octa-kagomé lattice are 3.150(0) Å and 3.069(6) Å, respectively, whereas the Mn1–Mn2 distance is 3.902(1) Å.

Figure 2. (a) The three-dimensional structure frameworks and (b) topological spin structures of Mn$_3$O(SeO$_3$)$_3$; (c,d) show the octa-kagomé and staircase-kagomé spin sublattices, respectively. Here the blue, green, light blue and pink polyhedra represent Mn1O$_6$, Mn2O$_6$, Mn3O$_6$ and SeO$_3$, respectively. Balls of the above colors represent Mn1, Mn2 and Mn3 ions, respectively.

Figure 3. Detailed linkages of five main superexchange pathways in Mn$_3$O(SeO$_3$)$_3$. (a) indicates $J_1$ to $J_4$ and (b) indicates $J_5$, respectively.

Figure 4a shows the temperature dependence of magnetic susceptibility $\chi(T)$ of Mn$_3$O(SeO$_3$)$_3$ measured at 0.1 T. Magnetic susceptibility increases with decreasing temperature; two peaks can be observed at $T_{N1} \sim 4.5$ K and $T_{N2} \sim 45$ K, showing AFM transitions. At high temperature (80–300 K) inverse susceptibility $\chi^{-1}(T)$ follows the Curie–Weiss law with a Weiss temperature of $\theta = -8.89$ K and a Curie constant of $C = 11.03$ emu·mol$^{-1}$·K. The effective magnetic moment is calculated to be $\mu_{\text{eff}} = 5.42(3) \mu_B$, obtained by $\mu_{\text{eff}}^2 = 8C/n$, where $n = 3$. This value of $\mu_{\text{eff}}$ is slightly smaller than the spin-only value of 5.91(6) $\mu_B$. 
for Mn$^{2+}$ (3d$^5$, high spin) and larger than the spin-only value of 4.89(9) μB for Mn$^{3+}$ (3d$^4$, high spin). As Mn ions are mixed-valent, the theoretical magnetic moment of the titled compound is $\mu_{\text{theo}} = 5.25(9)$ μB obtained by the equation $\mu^2_{\text{eff}} = [\mu^2_{\text{eff}} (\text{Mn}^{2+}) + 2\mu^2_{\text{eff}} (\text{Mn}^{3+})]/3$. The value of $\mu_{\text{eff}}$ is quite close to that of $\mu_{\text{theo}}$, confirming that Mn ions in the structure are mixed valence. The negative value of $\theta$ suggests the presence of dominative AFM interactions between neighboring Mn ions. Figure S3 shows the $\chi T$-$T$ curve, in which the value of $\chi T$ decreases with decreasing temperature, which is characteristic of typical AFM interactions. As shown in Figure 4b, the heat capacity data of Mn$_3$O(SeO$_3$)$_3$ show a $\lambda$-type peak at $T \approx 45$ K and a corner-type transition at 4.5 K, providing concrete evidence for the two long-range magnetic orderings observed in the magnetic susceptibility curves.

![Figure 4](image1.png)

**Figure 4.** (a) The magnetic susceptibility $\chi (T)$ of Mn$_3$O(SeO$_3$)$_3$ and its reciprocal. (b) The heat capacity of Mn$_3$O(SeO$_3$)$_3$. The green solid line indicates Curie-Weiss fitting.

To further investigate the magnetic properties of the system, magnetization ($M$) as a function of applied field ($H$) was observed at 30 K and 2 K. As shown in Figure 5, at 30 K, magnetization increased linearly with increasing field, and did not saturate at 9 T. Furthermore, no hysteresis or remanent magnetization was observed. These features of the $M$-$H$ curve suggest that the magnetic anomaly at $T \approx 45$ K is the onset of an AFM ordering. At 2 K, the magnetization ($M$) shows a linear increase in magnetization at low field, indicative of a characteristic AFM ground state. A clear change in slope in the magnetization is observed at approximately 4.5 T, indicating field-induced magnetic transition. Furthermore, no hysteresis can be observed on the $M$-$H$ curve.

![Figure 5](image2.png)

**Figure 5.** Isothermal magnetization ($M$) as a function of applied field ($H$) at 2 K and 30 K.
It is well-known that the magnetic properties of solid magnets are strongly related to their structural features. The three-dimensional manganese topological framework of Mn$_3$O(SeO$_3$)$_3$ is formed by the intersection of octa-kagomé lattices and staircase-kagomé lattices. Firstly, we know that the kagomé-like lattices containing equilateral or isosceles triangle sublattices may exhibit strong frustrated magnetic properties [19–21]. We note the value of frustration factor, $f = |\theta|/T_N \sim 0.20$, with Weiss temperature $\theta = -8.89$ K and Neel temperature $T_N \sim 45$ K, ruling out spin frustration in the system. It is well known that primary magnetic interactions originate from the superexchange of Mn-O-Mn. A detailed description of superexchange interactions is shown in Figure 2c,d and itemized in Table 1; there are five main magnetic exchange interactions, numbered $J_1$–$J_5$, within the three-dimensional spin-lattice according to the Goodenough–Kanamori–Anderson rules (GKA rules) [22]. There are two isosceles triangular topological configurations composed by $J_1$–$J_4$ on the staircase-kagomé spin sublattice. According to the GKA rules, $J_2$ and $J_3$ are AFM interactions. $J_1$ and $J_4$ both have two Mn-O-Mn superexchange interactions, as the corresponding MnO$_6$ octahedra share their edges. In general, the spin exchange parameter, $J$, can be written as $J = J_{FM} + J_{AFM}$, where $J_{FM}$ indicates ferromagnetic exchange and $J_{AFM}$ indicates antiferromagnetic exchange ($J_{FM} > 0$ and $J_{AFM} < 0$) [23]. So, $J_1 = J_{AFM(O6)} + J_{AFM(O5)}$, and the AFM interaction via O6 in $J_1$ is negligible; this means that $J_1 \approx J_{AFM(O5)} > 0$. Using the same analytical method, the spin exchange parameter, $J_5$, is ambiguous, as the magnitude of $J_{AFM(O7)}$ is difficult to calculate. $J_5$ should be a weak AFM interaction. This analysis indicates that AFM interactions are dominant in the system, which is consistent with the negative value of $\theta$. It is significant that the neighboring octa-kagomé sublattices are separated by [-Mn1-] chains and that the neighboring staircase-kagomé sublattices are connected by [Mn$_2$O$_{10}$] dimers. It is safely said that these two long-range magnetic orders are driven by interlayer magnetic coupling. It is noteworthy that [-Mn1-] chains are composed of Mn$^{2+}$ ions. If Mn$^{2+}$ ions are replaced with nonmagnetic ions with a radius similar to Mn$^{2+}$, such as Mg$^{2+}$ or Zn$^{2+}$ [24], an octa-kagomé lattice composed of Mn$^{3+}$ ions might form. The expected compounds may exhibit spin-liquid or other quantum physical properties [25,26].

Table 1. Geometric parameters of dominant magnetic superexchanges in Mn$_3$O(SeO$_3$)$_3$ *.

| $J_1$ | d(Mn-O) (Å) | d(Mn-Mn) (Å) | Mn-O-Mn Angle (°) | Magnetism |
|-------|-------------|-------------|-------------------|-----------|
| $J_1$ | Mn1-2.130(7)-O6-2.130(7)-Mn1 Mn1-2.361(4)-O5-2.361(4)-Mn1 | 3.332(9) | Mn1-O6-Mn1...102.90(8)AFM-w Mn1-O5-Mn1...89.77(1)FM-S | FM |
| $J_2$ | Mn3-1.857(1)-O7-1.857(1)-Mn3 | 3.332(9) | Mn3-O7-Mn3...127.61(5)AFM-S | AFM |
| $J_3$ | Mn1-2.361(4)-O5-2.278(1)-Mn2 | 3.902(1) | Mn1-O5-Mn2...114.49(4)AFM-S | AFM |
| $J_4$ | Mn2-2.049(5)-O3-2.310(4)-Mn3 Mn2-1.854(2)-O7-1.857(1)-Mn3 | 3.069(6) | Mn2-O3-Mn3...89.29(7)FM-S Mn2-O7-Mn3...111.59(8)AFM-S | ? |
| $J_5$ | Mn2-1.896(5)-O4-2.169(5)-Mn2 Mn2-2.169(5)-O4-1.896(5)-Mn2 | 3.150(0) | Mn2-O4-Mn2...101.34(9)AFM-w x 2 | AFM |

* The S or W behind AFM or FM (in the Mn-O-Mn Angle (°) column) refers to the magnitude of the $J$ value; S refers to strong and W refers to weak.
As shown in Figure 6, Mn$_3$O(SeO$_3$)$_3$ undergoes a slow weight gain of approximately 0.20% from 100 to 200 °C and a slow weight loss of approximately 0.40% from 300 to 400 °C. As the weight of the sample is only approximately 7 mg, slight weight gain/loss may be caused by instrument error. As the temperature rises, two successive steps of weight loss of approximately 57% occur from 450 to 630 °C, corresponding to the calculated 59% loss of 3SeO$_2$. The 2% difference may also be caused by instrument error. Based on this analysis, the final residues of Mn$_3$O(SeO$_3$)$_3$ should be Mn$_3$O$_4$; however, this was difficult to characterize, as the residues melted in the Al$_2$O$_3$ crucible after being heated to 900 °C. We re-selected the sample and sintered it in a smooth quartz crucible at 800 °C in a nitrogen atmosphere for 10 min. We then scraped off the sintered product and performed powder X-ray diffraction analysis. As shown in Figure S4, the residue was confirmed as Mn$_3$O$_4$ (PDF #80-0382). This result is consistent with the decomposition characteristics of most manganese-based compounds.

**Figure 6.** The thermogravimetric curve of Mn$_3$O(SeO$_3$)$_3$, which shows that the residual product of decomposition above 630 °C is Mn$_3$O$_4$.

4. Conclusions

A mixed-valence compound, Mn$_3$O(SeO$_3$)$_3$, was successfully synthesized using a conventional hydrothermal method. The reagent LiI acted as a mineralizer. Mn$_3$O(SeO$_3$)$_3$ was shown to have a channel structure with a three-dimensional magnetic topological framework formed by the intersection of octa-kagomé spin sublattices and staircase-kagomé spin sublattices. Magnetic and specific heat data confirmed that Mn$_3$O(SeO$_3$)$_3$ exhibits two successive long-range AFM orderings with $T_{N1} \approx 4.5$ K and $T_{N2} \approx 45$ K, and a field-induced spin–flop at a 4.5 T critical field at low temperature. Moreover, magnetic measurements confirmed that the ratio of Mn$^{2+}$/Mn$^{3+}$ ions in this compound is 1:2, which is consistent with the structural analysis. The exploratory synthesis of Mg$^{2+}$ or Zn$^{2+}$ replaced compounds is in progress.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/ma15165773/s1, Figure S1. Single crystals of Mn$_3$O(SeO$_3$)$_3$ obtained by a conventional hydrothermal method. Figure S2. The oxygen-coordination environments for (a) Mn1, (b) Mn2, (c) Mn3, (d) Se1, (e) Se2 and (f) Se3 atoms in Mn$_3$O(SeO$_3$)$_3$. Figure S3. The variation in $\chi T$ with the temperature of Mn$_3$O(SeO$_3$)$_3$. With the decreasing temperature, the value of $\chi T$ decreases. Figure S4. Powder X-ray diffraction pattern for the final residues of Mn$_3$O(SeO$_3$)$_3$ after sintered at 800 °C for 10 min in nitrogen atmosphere.
Author Contributions: W.Z. and G.Q. conceived and designed the experiments. W.Z. prepared the materials and performed the XRD and magnetism testing. J.T. performed the thermogravimetric measurement. P.J. carried out the selection of pure phase crystals. W.Z., M.C. and G.Q. analyzed the data. W.Z. and G.Q. wrote the paper. M.C., J.T., P.J. and X.L. edited the paper. All authors discussed the results and commented on the manuscript. All authors have read and agreed to the published version of the manuscript.

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