Powder Neutron Diffraction Measurements of One-dimensional Magnets $MPb_4Sb_6S_{14}$ (M = Fe, Mn)

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One-dimensional (1D) Heisenberg antiferromagnetic chain (HAF) compounds in magneto-chemistry and physics fields have attracted considerable interest, because most of them have been served as a prototypical model in quantum statics. Haldane theoretically predicted that 1D-HAF systems having integer spin quantum number ($S = 1, 2, \cdots$) should have a spin energy gap called as Haldane-gap between the ground state and the first excited state, in contrast to the case of half-integer spin quantum number ($S = 1/2, 3/2, \cdots$). [1] Since Haldane 's prediction, extensive studies have been carried out on 1D-HAF systems with integer S. In 1986, the first $S = 1$ compound with Haldane gap, $[Ni^{2+}(en)_2NO_2](ClO_4)$ (so called as NENP) was discovered by Renard and his co-workers as the real system. [2] After the discovery of this compound, some of $S = 1$ Haldane gap compounds have been studied. [3]

We propose the rare $S = 2$ Haldane candidate mineral semiconductor compound, $Fe^{2+}Pb_4^{2+}Sb_6^{3+}S_{14}^{2-}$ (Jamesonite, hereafter FPSS). It is the isomorphic compound of $Mn^{2+}Pb_4^{2+}Sb_6^{3+}S_{14}^{2-}$ (Bénavidésite, hereafter MPSS). The several properties (structural, thermal, optical, electrical, magnetic properties) and synthetic condition of these compounds, had been reported. [4, 5, 6, 7] The monoclinic crystal structures of FPSS and MPSS consist of the lozenge-shaped $[Pb_4Sb_6S_{13}]$ and the rod-shaped $[MS_6]$ substructures (Fig. 1). In the structure, Fe^{2+} (d^6; $S = 2$) is located at the origin site (Wyckoff position; 2*a* in $P2_1/a$) and octahedrally coordinated by six sulfur atoms. The $[FeS_6]$ octahedra form the edge-shared 1D linear chain, running along the c-axis, as shown in Fig. 1. The shortest Fe$\cdots$Fe distance is 4.030(4) Å within the chain and 12.388(6) Å between the chains. Therefore, the magnetic inter-chain interaction should be weak, and FPSS can be regarded as an ideal 1D magnetic chain system with $S = 2$. From these crystallographic and magnetic properties, FPSS is expected to be a candidate of $S = 2$ Haldane compound. Apart from the argument of $S = 2$ Haldane compound, $S = 2$ 1D magnetic chain compound itself is rare. In the magnetic susceptibility measurements, FPSS showed 1D HAF behavior with a broad peak around 33.5 K, where a high-spin state ($S = 2$) of Fe^{2+} was estimated from a Curie-Weiss law fitting of magnetic susceptibility. Under 10K, FPSS shows two anomalies at $\sim$ 8 K and $\sim$ 3 K. [4, 5, 6] On the other hand, MPSS shows a broad peak around 25 K, and in lower temperature range small Curie tail are observed. However, both FPSS and MPSS did not show any long range ordering behaviors from results of magnetic susceptibilities (AC and DC), heat capacity and Mössbauer measurements, both compounds showed spin-glass behavior under low temperature range. [5, 6, 7] In 2004, Léone *et al.* reported powder neutron measurement using natural FPSS, and they observed extra peaks to be caused by magnetic long-range ordering. [8] The result is not consistent with our results. In this study, we carried out neutron powder-diffraction measurements using synthesized FPSS and MPSS compounds to understand magnetic behaviors these compounds.

The samples were prepared by solid-state reaction. [5] The neutron powder-diffraction measurement ($7^\circ \leq 2\theta < 157^\circ$)

was carried out using IMR-HERMES diffactmetor (T1-3), installed in the JRR-3M reactor. The wavelength of neutron was 1.8265(1) Å, which was vertically focused by a (331) Ge monochromator. The intensity data was observed at 4.0 K for FPSS and 1.4 K for MPSS, respectively.

Around 15.5° in 2θ, weak peaks are observed, but they are not matched with Léone's proposed magnetic ordering model. [8] To understand the details of magnetic behaviors of the compounds we need to examine under lower temperature with the higher resolution facilities.

References

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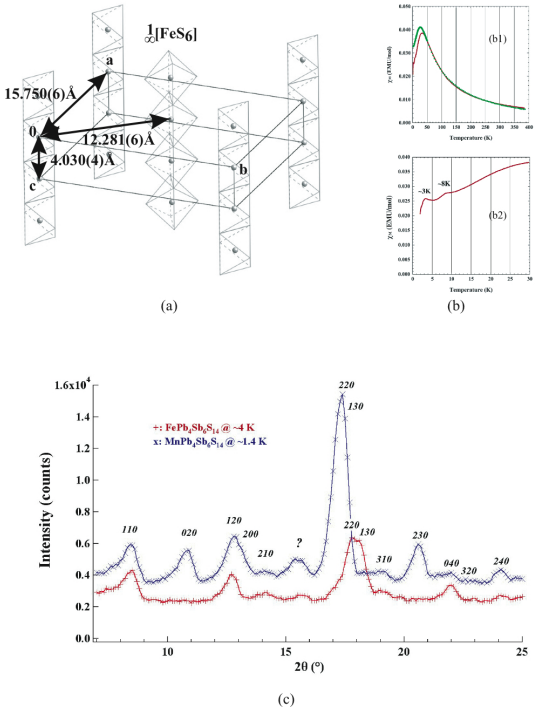

Fig. 1. 1) 1D-chain structure in FPSS. 2) Magnetic susceptibility of FPSS. 3) Neutron powder-diffraction diagram.