Crystal Structure and Magnetism of Natural Mineral Henmilite from Fuka Mine, Okayama Prefecture

We have studied the crystal structure and magnetic properties of natural mineral henmilite, $Ca_2Cu(OH)_4[B(OH)_4]_2$, which is a blue calcium copper borate mineral found only in the Fuka Mine, Okayama Prefecture, Japan. Heat capacity measurements revealed that a dome-shaped antiferromagnetic ordering region exists in the temperature–magnetic-field phase diagram. Such behavior indicates the presence of quantum spin fluctuations. We have determined the precise crystal structure of henmilite using synchrotron X-ray diffraction experiments at BL-14A. The obtained crystal structure in combination with DFT calculations suggests that the henmilite has a coupled two-leg ladder magnetic lattice, which causes the quantum spin fluctuations.

Natural minerals, created by the earth's activity since ancient times, have more diverse crystal structures than artificially synthesized inorganic compounds. Since the diversity of crystal structures leads to the diversity of properties exhibited by materials, the magnetic properties exhibited by natural minerals have long attracted the interest of scientists. We have focused our attention on natural minerals from Japan. In the Japanese Archipelago, more than 140 kinds of new minerals have been discovered so far. However, due to the rarity of the minerals, there have been few magnetic studies from the viewpoint of solid-state physics.

Henmilite is one of the most famous new minerals from Japan, which is found only in the Fuka Mine in Okayama Prefecture. Henmilite was first reported in 1986 and its chemical formula is $Ca_2Cu(OH)_4[B(OH)_4]_2$ [1, 2]. The divalent copper ions responsible for magnetism are arranged in a distorted two-dimensional square lattice. Spin-1/2 low-dimensional antiferromagnets have been widely studied because of their potential to exhibit fascinating properties caused by quantum effects. In this work, the crystal structural features and magnetic behavior of henmilite are reported [3].

As a first step to study the crystal structure and magnetism of henmilite, single-crystal X-ray diffraction experiments were performed at BL-14A and BL-8B. In these experiments, superlattice reflections were observed, which correspond to (1/2*h k l*) with the lattice constant reported previously. Precise analysis of the crystal structure revealed that the superlattice structure is formed by antiferroelectric arrangement of hydrogen-bond chains. The determined crystal structure is shown in Fig. 1(a). This structural feature affects the magnetic nature of henmilite: there are three Cu-Cu bond distances: short (~5.65 Å), intermediate (~5.73 Å), and long (~5.81 Å), which are expected to be closer to a two-leg ladder system than to a square lattice one. We performed DFT calculations from the obtained crystal structures to estimate the magnetic exchange interactions. The results indicated the nature of the coupled two-leg ladder antiferromagnet, as shown in Fig. 1(b). Interestingly, the position of the hydrogen atoms also affects the strength of the magnetic interactions.

In the magnetic susceptibility measurements of henmilite, a broad peak at approximately 3 K, reflecting the low-dimensional antiferromagnetic interaction, was observed. To further investigate the presence of magnetic phase transition at lower temperatures, specific heat measurements down to 0.1 K were performed. An antiferromagnetic phase transition occurred at ~0.2 K at 0 T, and this transition shifted to higher temperatures with the application of magnetic fields, reaching ~0.8 K at 3 T. At higher magnetic fields, the transition temperature decreased and no phase transition occurred above 9 T. As a result, a dome-shaped antiferromagnetic region appeared in the magnetic field–temperature phase diagram, as shown in Fig. 1 (c). Such a feature is not observed in ordinary antiferromagnets, but has been reported in low-dimensional antiferromagnets with quantum spin fluctuations. Strong quantum spin fluctuations are expected in the spin system of henmilite because the two-leg ladder system is known to be a spin-gap system [4]. The application of magnetic fields suppresses the fluctuation and increases the magnetic phase transition temperature, resulting in the appearance of a dome-shaped antiferromagnetic region.

In this study, advanced synchrotron X-ray experiments and physical property measurements were performed on a natural mineral from Japan. Considering the diversity of crystal structures of natural minerals, there are likely to be many other minerals that exhibit novel phenomena.

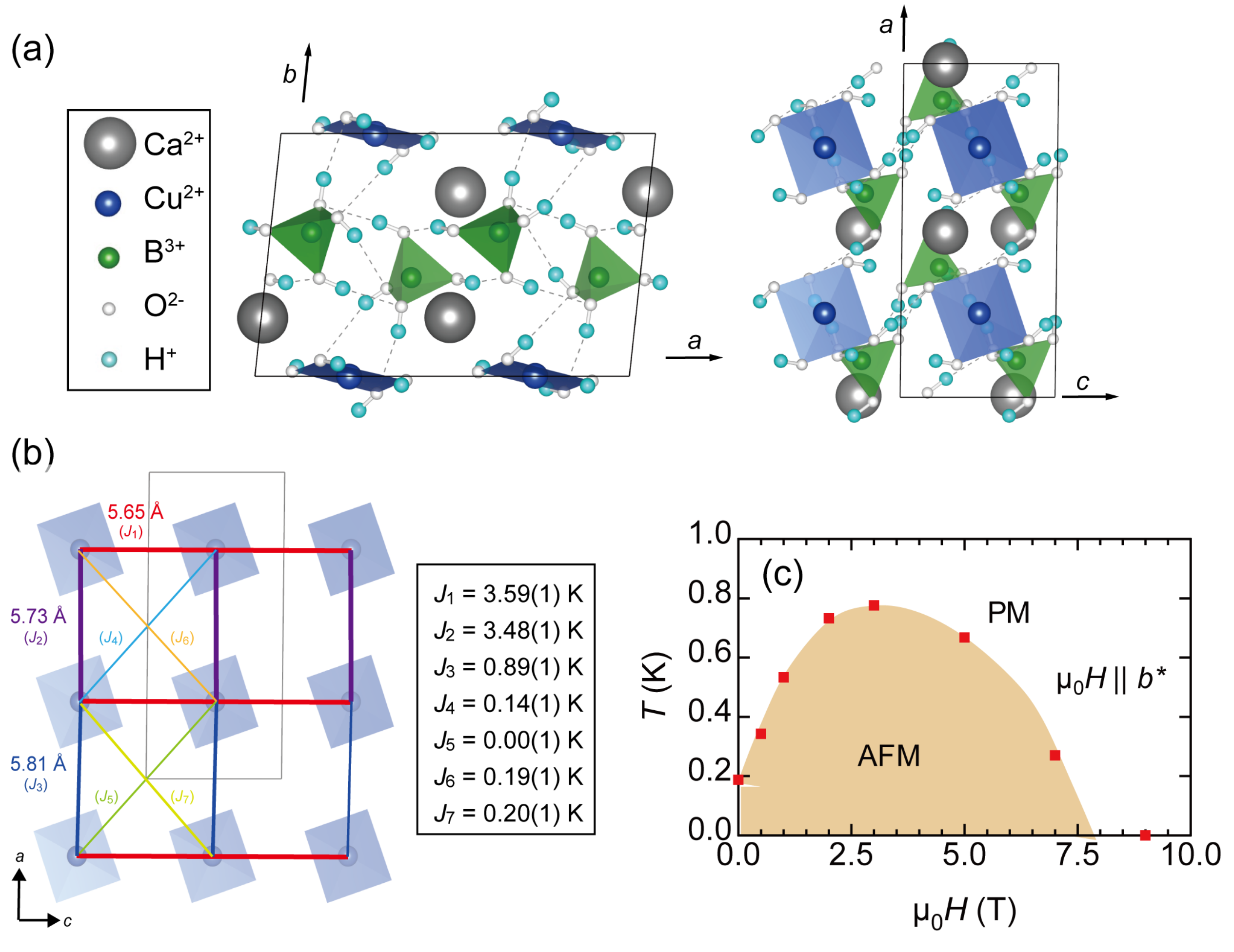

Figure 1: (a) The obtained crystal structure of henmilite. The structure is viewed along [001] (left) and [010] (right). The crystal structures were drawn using VESTA software. **(b)** Cu-Cu distances and strengths of magnetic exchange interactions estimated from the DFT calculation. **(c)** Magnetic phase diagram of henmilite. AFM and PM denote antiferromagnetic and paramagnetic regions, respectively.

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BEAMLINES

BL-14A and BL-8B

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