論 文 の 内 容 の 要 旨

論文題目 Crystal Chemistry and Frustrated Magnetism of Kagome Minerals

（カゴメ格子無機化合物の結晶化学とフラストレート磁性）

氏　　名　　石川　孟

1. Introduction

Searching for exotic quantum states in materials is a challenge in the recent condensed matter physics. Frustrated magnets, where conventional magnetic orders are suppressed owing to magnetic frustration, have attracted much attention as a playground for realizing quantum states such as spin liquids and spin nematics [1]. Magnetic frustration is caused either by the geometry of spins coupled by antiferromagnetic interactions or by competitions between ferromagnetic and antiferromagnetic interactions (Fig. 1(a)). A typical example for the former case is the spin-1/2 Heisenberg antiferromagnet on the two-dimensional kagome lattice made of corner sharing triangles. Theoretical studies have predicted spin liquid ground state and successive magnetic field induced phase transitions [2]. A typical example of the second type of frustration is the quasi one-dimensional magnet with a ferromagnetic nearest-neighbor (NN) coupling J_1 competing with an antiferromagnetic next-nearest-neighbor (NNN) coupling J_2 along the chain. This system is expected to show a helical spin order in low magnetic fields, a spin density wave (SDW) order in medium fields, and a spin nematic order in high fields just below the saturation of magnetization [3]. Spin nematic order, which corresponds to a multipolar order associated with bound magnon pairs, has been extensively searched in recent experiments.

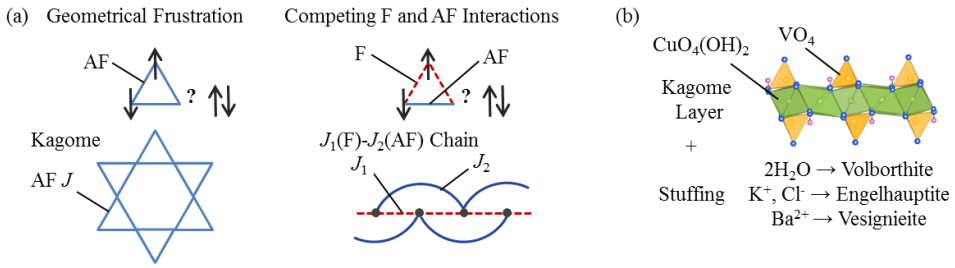

Figure 1. (a) Examples of frustrated magnets: antiferromagnetic (AF) and Ferromagnetic (F) interactions are shown by solid and dashed lines, respectively. (b) Structural features of kagome minerals studied in this work.

One problem in the experimental studies of frustrated magnets is the presence of the disorder in real materials: frustrated magnets are sensitive to small perturbations and the true ground state can be replaced by randomly frozen states like spin glasses. Another problem is the difficulty in obtaining high-quality single crystals with relatively large size that are required for detailed magnetic studies. In search for novel magnetic states, we have studied three copper minerals: volborthite $Cu_3V_2O_7(OH)_2 \cdot 2H_2O$, engelhauptite $KCu_3V_2O_7(OH)_2Cl$, and vesignieite $BaCu_3V_2O_8(OH)_2$, which are closely related in the crystal structures [4]. These minerals have common layers made of edge sharing $CuO_4(OH)_2$ octahedra decorated by VO_4 tetrahedra, in which Cu^{2+} ions form regular or distorted kagome lattices (Fig. 1(b)). There are H_2O molecules in volborthite, K^+ and Cl^- ions in engelhauptite, and Ba^{2+} ions in vesignieite between the kagome layers. We have successfully synthesized high-quality single crystals or powder

samples, characterized their crystal structures by X-ray diffraction (XRD) method, and investigated their magnetic properties in wide temperature and magnetic field ranges. Based on thus obtained data, we have developed the crystal chemistry of the kagome minerals and clarified their unusual magnetic properties.

2. Results

2.1. Orbital Arrangements and structural phase transitions in volborthite and engelhauptite

We have found two structural phase transitions at around 290 and 155 K and two new structures of volborthite in the single crystal XRD measurements. Above 290 K, the *C*2/*c* structure, which is a superstructure with doubled *c*-axis compared to the previously reported *C*2/*m* structure, is found [5]. It undergoes a first order transition around 290 K into an *I*2/*a* structure. At 155 K, another transition into a $P2_1/a$ structure is observed. Structural analysis of the synthetic powder sample of engelhauptite $KCu_3V_2O_7(OH)_2Cl$ reveals a monoclinic structure with space group $P2_1/m$, which is different from the hexagonal structure reported in the natural mineral.

These different structures are distinguished by the arrangement of spin carrying orbitals in the kagome layers (Figs. 2(a-c)). A common feature of volborthite and engelhauptite is the presence of chains made of d_{x2-y2} orbitals (vertical rows in Figs. 2(a-c)). The difference between them is the arrangements of orbitals between the chains. In the high temperature *C*2/*c* structure of volborthite and engelhauptite, d_{x2-y2} orbitals are selected and arranged with the same direction, while d_{3z2-r2} orbitals are selected in the previous *C*2/*m* structure (Fig. 2(a,c)). In the low temperature *I*2/*a* and $P2_1/a$ structures, the d_{x2-y2} orbitals have a staggered arrangement (Fig. 2(b)). The transition between the *C*2/*c* and *I*2/*a* structures of volborthite can be called an orbital flipping transition. On the other hand, the structural difference between the *I*2/*a* and $P2_1/a$ structures are tiny. Structural analyses revealed different orbital arrangements and the phase transitions are caused by the cooperative structural changes in the Jahn-Teller distortions of $CuO_4(OH)_2$ octahedra, tilts of VO_4 tetrahedra, and the arrangements of the H_2O molecules.

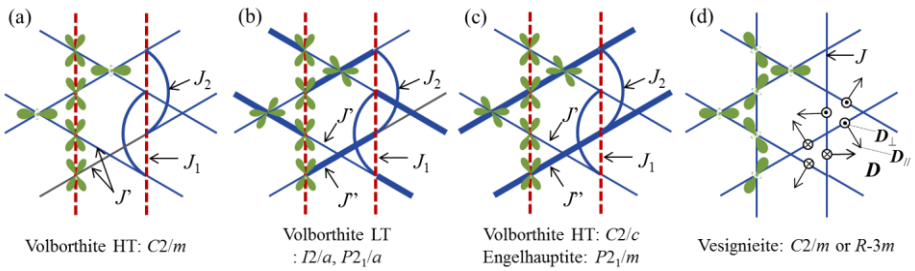

Figure 2. Orbital arrangements projected onto the kagome plane and the patterns of magnetic interactions of the materials studied in this thesis.

2.2. High-Field Magnetization Processes of Volborthite and Engelhauptite

The previous powder sample of volborthite showed magnetization steps at 4.5, 26, and 46 T and a saturation behavior above 50 T, of which nature is unclear. Surprisingly, the magnetization curves of the single crystals increases steeply around 25 T, where the second magnetization step is observed in the powder sample, and then saturates followed by a small increase up to 74 T (Fig. 3(a), [6]). The saturation moment is close to the 1/3 of the full moment, i.e. the phase above 30 T is the 1/3 plateau. Moreover, a novel magnetic phase is found between 23 and 26 T in the single crystals; the field derivative of magnetization shows unusual flat maximum there. The phase

is also observed in the magnetocaloric effect measurements. In the magnetization curve of engelhauptite (Fig. 3(b)), on the other hand, no anomaly is observed around 25 T, where volborthite shows a transition to the 1/3 plateau phase, but the saturation behavior above 50 T, which is similar to the third magnetization step in the powder samples of volborthite, is observed.

From the structural parameters in the low temperature structure of volborthite, ferromagnetic NN coupling along the chain direction, J_1, antiferromagnetic NNN coupling J_2, and antiferromagnetic interchain couplings via intervening Cu ions, J' and J" as shown in Fig. 2(b) are expected. In this pattern of magnetic interactions, a ferrimagnetic state, where the J_1–J_2 chains are polarized with the oppositely polarized intervening spins is expected at the 1/3 plateau phase. Moreover, NMR experiments of volborthite single crystals have shown that the spin structure below 23 T is a collinear SDW state [6]. These results remind us the phases predicted in the J_1–J_2 chain system, i.e. helical, SDW, nematic orders, and the saturated states of the chains occur with increasing magnetic field, and suggest a possibility that the phase at 23-26 T in volborthite have a nematic order.

Although volborthite and engelhauptite have the J_1-J_2 chain like orbital arrangements in common, their magnetization processes are completely different. This result suggests that the arrangement of J' and J", which is determined by the orbital arrangement between the J_1-J_2 chains, is crucial for the high field phases of these materials. This is consistent with the spin model proposed in the recent theoretical study, which predicts the realization of nematic phase in volborthite [7]. Moreover, the large sample dependences of volborthite are considered to be caused by the disorder in the orbital arrangement between the J_1-J_2 chains.

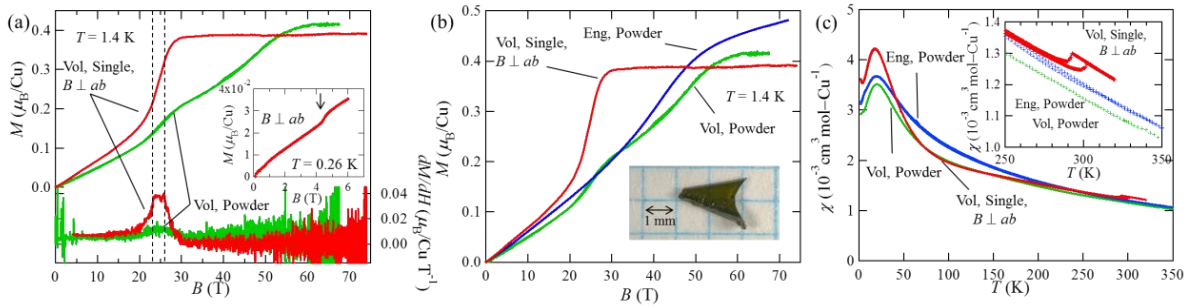

Figure 3. (a) Magnetization curves and their magnetic field derivatives of volborthite (vol) [6]. (b) Magnetization curves and (c) magnetic susceptibility of volborthite and engelhauptite (eng).

2.3 Topochemical Synthesis of Vesignieite and Engelhauptite

I have succeeded in crystal-to-crystal transformations of volborthite completely into vesignieite by hydrothermal reaction (Fig. 4(a)). Thus obtained crystals of vesignieite, which has almost perfect kagome lattice, enable magnetic anisotropy measurements not performed so far. An antiferromagnetic order at 9 K and a large anisotropy below 25 K is observed (Fig. 4(b)). In the antiferromagnetically ordered temperature region, a weak-ferromagnetic moment is observed within the kagome plane. These results are explained by the Dzyaloshinskii-Moriya (DM) interaction with a D-vector having dominant out-of-plane component ($D_\perp$ in Fig. 2(d)).

Two phase transitions are observed at 5 and 40 T in the magnetization curve. The transition at 5 T is considered to be a spin flop like transition. At 40 T, the slope of magnetization curve becomes smaller, but the magnetization continues to increase up to 72 T (Fig. 4(c)), instead of the 1/3 plateau expected for the spin-1/2 Heisenberg

kagome antiferromagnet. I consider that the relatively large DM interactions suppress the 1/3 plateau state and stabilize another magnetic state in vesignieite in the high magnetic field region.

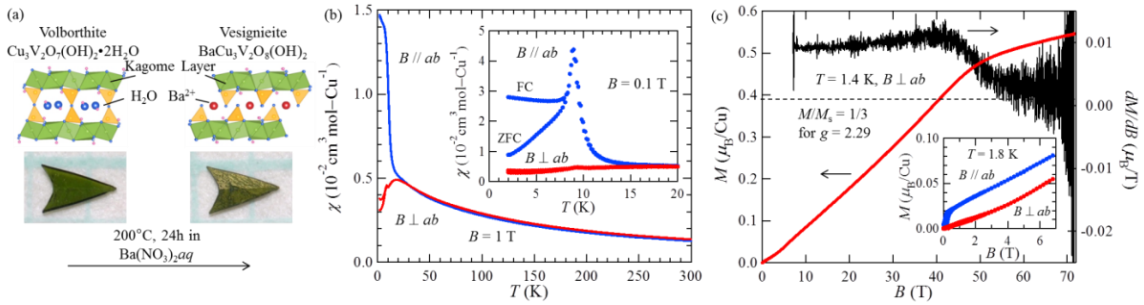

Figure 4. (a) Crystal structures and photographs of crystals before and after topochemical reaction from volborthite into vesignieite. (b) Magnetic susceptibility and (c) magnetization curves of the crystals of vesignieite.

3. Summary

I have successfully synthesized the crystals of kagome minerals by the conventional hydrothermal method and a novel topochemical route. Structural analyses revealed various orbital arrangements in the kagome layers depending on the types of ions or molecules between the layers and novel phase transitions.

I have found a huge 1/3 magnetization plateau and a preceding novel phase which is considered to be related to the spin nematic order realized by the frustrated ferromagnetic and antiferromagnetic interactions in volborthite. Comparisons in the structural and magnetic properties between engelhauptite and volborthite revealed that the orbital order and disorder at the interchain Cu site change the magnetic properties drastically.

Topochemically obtained crystals of vesignieite have enabled the magnetic anisotropy measurements. Large magnetic anisotropy at low fields and a novel magnetic phase at high fields, which is different from the 1/3 plateau state, are observed. These may be attributed to the large DM interactions in the nearly perfect kagome lattice.

My findings in the crystal chemistry and magnetic properties of kagome minerals would stimulate further materials exploration in the field of frustrated magnetism and lead to the discovery of exotic magnetic phases.

References

1. L. Balents, Nature 464, 199 (2010). O. A. Starykh, Rep. Prog. Phys. 78, 052502 (2015).
2. S. Yan, D. A. Huse, and S. R. White, Science 332, 1173 (2011). S. Nishimoto, N. Shibata, and C. Hotta, Nat. Commun. 4, 2287 (2013).
3. Hikihara, L. Kecke, T. Momoi, and A. Furusaki, Phys. Rev. B 78,144404 (2008). M. E. Zhitomirsky and H. Tsunetsugu, Europhys. Lett. 92, 37001 (2010).
4. R. Basso, A. Palenzona, and L. Zefiro, Neues Jahrb. Miner. Monatsh. 9, 385 (1988). M. Zhesheng, H. Ruilin, and Z. Xiaoling, Acta Geologica Sinica 4, 145 (1991). I. V. Pekov, O. I. Siidra, N. V. Chukanov, V. O. Yapaskurt, S. N. Britvin, S. V. Krivovichev, W. Schüller, and B. Ternes, Mineral. Mag. 77, 2695 (2013).
5. H. Ishikawa, J. Yamaura, Y. Okamoto, H. Yoshida, G. J. Nilsen and Z. Hiroi, Acta Crystallographica Section C: Crystal Structure Communications 68, i41 (2012). H. Yoshida, J. Yamaura, M. Isobe, Y. Okamoto, G. J. Nilsen, and Z. Hiroi, Nat. Commun. 3, 860 (2012).
6. H. Ishikawa, M. Yoshida, K. Nawa, M. Jeong, S. Krämer, M. Horvatić, C. Berthier, M. Takigawa, M. Akaki, A. Miyake, M. Tokunaga, K. Kindo, J. Yamaura, Y. Okamoto, and Z. Hiroi, Physical Review Letters 114, 227202 (2015).
7. O. Janson, S. Furukawa, T. Momoi, P. Sindzingre, J. Richter, and K. Held, arXiv:1509.07333 (2015).