

Quantum Magnetism in Kamchatkan Copper Minerals

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Quantum spin states in low-dimensional magnetic materials have been extensively studied because of emergent spin gaps and topological features. Intensive studies of one-dimensional linear spin chain antiferromagnets have succeeded in capturing several quantum spin states, such as the Tomonaga-Luttinger spin liquid state and the Haldane state. However in many cases, the lack of suitable model materials of theoretical models has hindered the observation of exotic quantum spin states. In the study of low-dimensional quantum magnets, minerals are often employed as model materials. For example, azurite ($\text{Cu}_2(\text{CO}_3)(\text{OH})_2$)¹⁾ and herbertsmithite ($\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$)²⁾ have been identified as candidates for the diamond chain (1D) and kagome lattice (2D) antiferromagnet, and many experimental studies have been performed. In this presentation, I will present results of comprehensive studies of magnetism in Kamchatkan copper minerals fedotovite³⁾ and atlasovite⁴⁾.

Fedotovite $\text{K}_2\text{Cu}_3\text{O}(\text{SO}_4)_3$ is a candidate of new quantum spin systems, in which the edge-shared tetrahedral (EST) spin clusters consisting of Cu^{2+} are connected by weak intercluster couplings forming a one-dimensional array (Fig. 1(a)). Comprehensive experimental studies by magnetic susceptibility, magnetization, heat capacity, and inelastic neutron scattering measurements reveal the presence of an effective $S = 1$ Haldane state below $T \cong 4$ K. Rigorous theoretical studies provide an insight into the magnetic state of $\text{K}_2\text{Cu}_3\text{O}(\text{SO}_4)_3$: an EST cluster makes a triplet in the ground state and a one-dimensional chain of the EST induces a cluster-based Haldane state (Fig 1(b)).

Atlasovite $\text{KCu}_6\text{AlBiO}_4(\text{SO}_4)_5\text{Cl}$ is a first candidate of a square kagome lattice spin-1/2 antiferromagnet (Fig. 2). The μSR measurement shows no long-range ordering down to 58 mK, roughly three orders of magnitude lower than the nearest neighbor interactions. The INS spectrum exhibits a streak-like gapless excitation and flat dispersionless excitation, consistent with powder-averaged spinon excitations. Our experimental results strongly suggest the formation of a gapless QSL in $\text{KCu}_6\text{AlBiO}_4(\text{SO}_4)_5\text{Cl}$ at very low temperature close to the ground state.

I will also discuss why I focused on Kamchatkan copper minerals as candidates for exotic quantum magnets.

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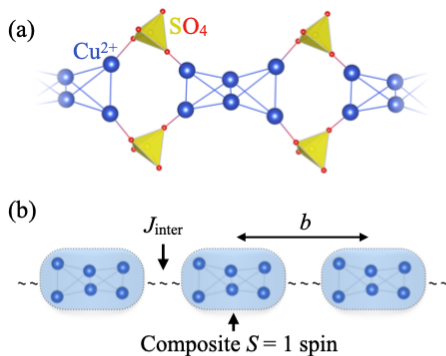


Fig. 1: (a) Crystal structure of $\text{K}_2\text{Cu}_3\text{O}(\text{SO}_4)_3$. The edge-shared tetrahedral spin cluster of the Cu^{2+} ions (blue) displayed with nearby oxygen (red) and sulfur (yellow) ions. (b) Schematic effective model of cluster-based $S = 1$ Haldane chain.

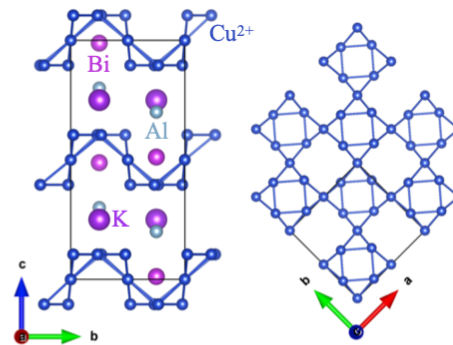


Fig. 2: Crystal structure of $\text{KCu}_6\text{AlBiO}_4(\text{SO}_4)_5\text{Cl}$. The square kagome lattice of the Cu^{2+} ions (blue) displayed with nearby nonmagnetic ions.

Discovery of Magnetocaloric Materials by Machine Learning

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The liquefaction of hydrogen gas using the magnetocaloric effect (MCE) is expected for the development of hydrogen society to prevent the global warming. The magnitude of the magnetic entropy change (ΔS_M) tends to peak at a material's magnetic ordering temperature, such as Curie temperature, and its maximum value for a ΔH strongly depends on the material itself. Thus, it is highly desired to discover suitable materials showing marked MCE in the working temperature range. However, it still remains challenging to explore and design new materials that can exhibit a remarkable MCE. To tackle this issue, we constructed a machine learning (ML) model for predicting ΔS_M^{MAX} only based on the applied field change and chemical formula of the materials. We used the gradient boosting method as implemented in XGBoost [1] package, and optimized hyperparameters in the ML model using HyperOpt [2], and obtained a best model that gives a mean absolute error of 1.8 (J kg⁻¹ · K⁻¹) for the test dataset and R² = 0.85 as depicted in Fig. 1. Then, we applied this ML model in conjunction with our domain expertise to filter possible candidates for experimental verification. Through this approach, we synthesized the most promising candidate and experimentally found that HoB₂ exhibits ΔS_M^{MAX} of 40 J kg⁻¹ K⁻¹ (0.35 J cm⁻³ K⁻¹) for a field change of 5 T [3], to our knowledge the highest value among all known bulk second-order phase transition solid magnets in this temperature range as shown in Fig. 2. Therefore, the discovered material HoB₂ would be highly suitable for liquefaction of hydrogen gas.

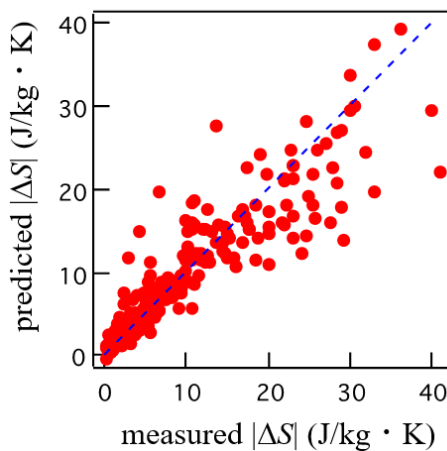


Fig. 1 ML model for prediction of magnetocaloric materials.

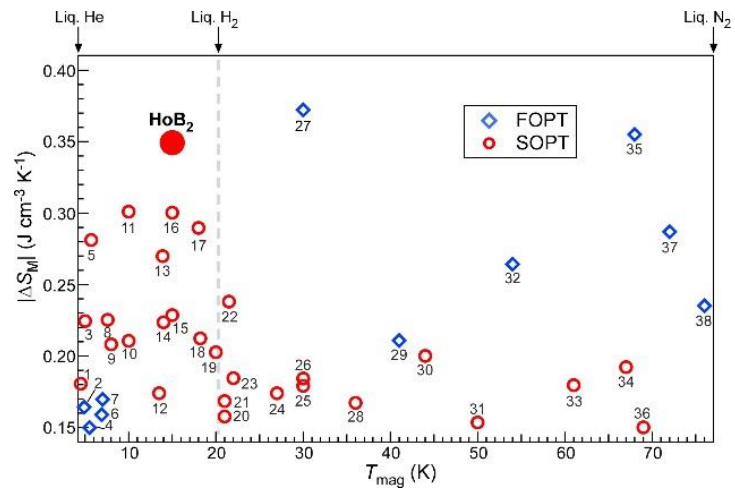


Fig. 2 Comparison of ΔS of HoB₂ with current known magnetocaloric materials between 4.2 to 77 K

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Search for new superconductors

using bulk combinatorial chemistry method

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Effective methodologies for developing innovative, high-performance materials are essential for sustaining materials research in Japan, where the human resources are shrinking. We have been testing whether new superconductors (SCs) can be discovered efficiently using the concept of combinatorial chemistry (CC) ¹, which has a successful history in the field of drug discovery. Keys to the success of CC are the simultaneous synthesis of many compounds and high-throughput screening to extract substances with the desired function.

Figure 1 shows the protocol for searching for new SCs by the CC method (called the bulk combinatorial (BC) method because bulk samples are used). A sample consisting of many compounds is prepared by heating a pellet with randomly selected elements for a short period of time (the simultaneous synthesis of many compounds). Because of the huge diamagnetic response associated with the superconducting transition, even a small fraction (~0.01%) of new SCs accidentally formed in the pellet can be detected by a high-sensitive magnetometer (high-throughput screening).

Figure 2 shows the examples of SCs discovered by the BC method ². SCs with various structure types were found. Some SCs would not have been synthesized without the BC method. Unexpected discoveries are another advantage of the BC method. Through this study, we are convinced that the BC method is a very efficient method to find new SCs.

We believe that the BC method can be applied not only to SCs but also to other functional materials. It is then important to find high-throughput screenings suitable for the material's properties. Furthermore, the BC method has the potential to grow into an even more powerful method by combining materials informatics to determine more promising starting elements and sample preparation conditions etc.

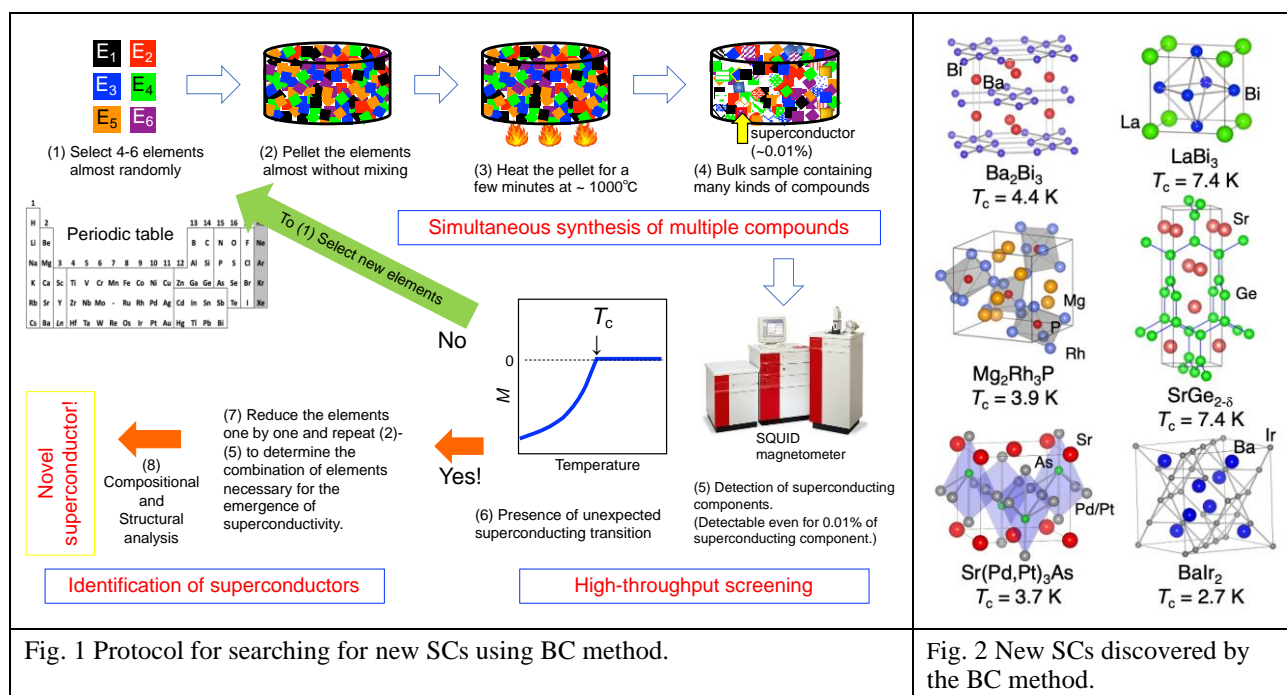


Fig. 1 Protocol for searching for new SCs using BC method.

Fig. 2 New SCs discovered by the BC method.

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Intercalation compounds of 1D-structured transition metal trichalcogenides

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In general, intercalation into two-dimensional (2D) materials is well known to induce lattice expansion. However, in the case of one-dimensional (1D) materials, the effect of intercalation on the structure and physical properties is not understood comprehensively. Transition metal trichalcogenides (TMTs) are typical 1D materials and comprise 1D trigonal prismatic units surrounded by van der Waals gap. This three-dimensionally spread van der Waals gap can accommodate three equivalents or more guest ions, although the capacity of 2D material is only one equivalent in general. Based on such a high ion accommodating capacity, 1D materials are expected to show various functionality. However, the detailed crystal structure of 1D materials after intercalation has not been experimentally revealed because it is challenging to intercalate guest ions into 1D materials while maintaining high crystallinity.

In this study, Ag ions were intercalated into ZrTe_3 , which is a member of the TMT family with a 1D structure, via a proton-driven ion introduction (PDII)(Fig. 1): solid-state intercalation process¹⁾. The change in crystal structure and physical properties according to Ag concentration were clarified for the first in our study. Here, six essential novel findings of TMT intercalation compounds are listed below.

- 1D trigonal prismatic structure in ZrTe_3 changed to 1D octahedral structure via Ag intercalation using PDII. During the structural transition, the long-range order of crystals was disrupted, despite the retention of the 1D order. This unique state was referred to as a “quasi-amorphous phase” in this study.
- The formation of the quasi-amorphous phase affords a reasonable explanation for the previously reported contradiction that the crystal structure did not change in the initial stage of intercalation into TMTs²⁾.
- The quasi amorphous phase shows the homogeneous Ag concentration in the macroscopic region via SEM-EDS measurements but inhomogeneous Ag concentration in the nanoscale region via STEM-EDS measurements. DFT calculations indicated that the origin of the nanoscale Ag inhomogeneity is the attractive interaction between Ag ions.
- In the quasi-amorphous phase, the electric properties changed continuously from superconductivity to semiconductivity according to the Ag concentration. In particular, the highest T_c (6.3 K) and B_{c2} (12 T) were obtained in $\text{Ag}_{0.5}\text{ZrTe}_3$ among TMT intercalation compounds. The nanoscale Ag inhomogeneity explains the enhancement of B_{c2} and the coexistence of both CDW and bulk superconductivity reported so far³⁾.
- Due to the attraction between Ag ions, the activation energy for pair diffusion of Ag ions is much lower than that for single diffusion. The former is less than 0.05 eV along the b -axis. This material should show anisotropic fast Ag ion diffusion.
- Judging the attraction or repulsion between guest ions in TMTs would predict whether to induce a quasi-amorphous phase or simple lattice expansion like 2D materials. A current overview of TMT intercalation compounds was presented based on this interaction between guest ions.

The quasi-amorphous phase with the 1D order is the state of matter based on a novel concept. It has the potential to open a pathway to achieve high functionality, such as fast ion diffusivity for low activation energy, a low thermal conductivity derived from the phonon scattering in a quasi-amorphous state, and high controllability of the electric carrier density based on the high guest-ion accommodation capacity.

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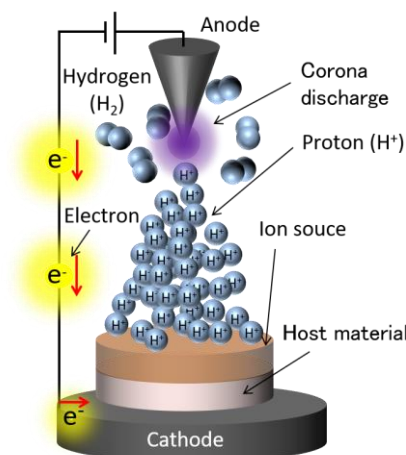


Figure 1. Schematic of PDII.

Layered ruthenium and iridium oxyfluoride thin films fabricated via topochemical fluorination

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Layered ruthenium and iridium oxyfluorides have various crystal structures and oxidation states and exhibit unique physical properties. We fabricated phase-pure and single-crystalline thin films of $\text{Sr}_2\text{RuO}_3\text{F}_2$, $\text{Ca}_2\text{RuO}_{2.5}\text{F}_2$, and $\text{Sr}_2\text{IrO}_{2.5}\text{F}_3$ via topochemical fluorination of Sr_2RuO_4 , Ca_2RuO_4 , and Sr_2IrO_4 using polyvinylidene fluoride and investigated their structures, electronic states, and electron transport properties [1-4]. All the fluorinated films exhibited a largely expanded c -axis than the precursors, indicating that fluorine ions are preferentially inserted into the SrO or CaO rocksalt blocks in the perovskite structures and that the oxygen atoms in the precursor oxides were partially removed upon fluorination. The X-ray photoemission spectroscopy, transmission electron microscope, and density functional theory revealed that $\text{Sr}_2\text{RuO}_3\text{F}_2$ is a Mott insulator with Ru^{4+} states and has two inequivalent F^- sites in the SrO layers [1,2]. On the other hand, $\text{Ca}_2\text{RuO}_{2.5}\text{F}_2$ thin films had the Ru^{3+} state and only one F^- site in the CaO rock-salt blocks [3]. This discrepancy is probably due to the larger lattice distortion in the Ca_2RuO_4 precursor than Sr_2RuO_4 . Both $\text{Sr}_2\text{RuO}_3\text{F}_2$ and $\text{Ca}_2\text{RuO}_{2.5}\text{F}_2$ films were insulating, with resistivity (ρ) of $4.1 \times 10 \text{ } \Omega \text{ cm}$ and $8.6 \times 10^{-2} \text{ } \Omega \text{ cm}$ at 300 K, respectively [1,3]. Moreover, the temperature behavior of ρ of $\text{Ca}_2\text{RuO}_{2.5}\text{F}_2$ thin film was well described by the two-dimensional variable range hopping model [3]. Optical and photoemission measurements of $\text{Sr}_2\text{IrO}_{2.5}\text{F}_3$ thin films revealed that the effective total angular momentum $J_{\text{eff}} = 3/2$ is stabilized upon fluorination owing to the large electronegativity of fluorine [4]. The $\text{Sr}_2\text{IrO}_{2.5}\text{F}_3$ film exhibited a semiconducting behavior described by Efros-Shklovskii variable-range hopping [4]. These results will be useful for modifying electronic states by anion doping to explore unprecedented physical properties in Ruddlesden-Popper-type oxides.

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