

Supporting Information

Frustrated Magnetism in the $S = 1$ Kagome Lattice

BaNi₃(OH)₂(VO₄)₂

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General Considerations

Unless otherwise stated, all chemicals were used as received from commercial sources, and all reactions were performed in air. All water used was ultrapure (type 1) H₂O (>18.2 MΩ-cm at 25 °C). Powder x-ray diffraction patterns were collected on a PANalytical X'Pert Pro instrument using Cu K_α radiation ($\lambda = 1.5403 \text{ \AA}$) with a Ni foil K_β attenuator and a silicon high-speed strip detector. The data were processed and fit using Rietveld techniques.

Magnetization measurements

Magnetization measurements were performed at the MIT Center for Materials Science and Engineering Shared Experimental Facility on a Quantum Design Magnetic Properties Measurement System (MPMS-XL). The sample was secured in a commercial straw having been measured to have negligible magnetic contribution, due to its symmetry. The magnetic susceptibility was calculated from the magnetization using the approximation $\chi \approx M/H$, where M is the measured magnetization, H is the applied magnetic field, and χ is the susceptibility. This approximation is valid in the paramagnetic region. The Curie-Weiss temperature was extracted from fits to the high temperature portion of the data, 100-300 K, using the relation,

$$\frac{1}{\chi} = \frac{1}{C}T - \frac{\theta_{CW}}{C}$$

where T is the temperature, C is the Curie-Weiss constant, and θ_{CW} is the Weiss temperature. Additional magnetic measurements were obtained on a Quantum Design Physical Properties Measurement System (PPMS). Samples were prepared in the same way as for the MPMS samples and the data were treated in the same way.

Additional magnetic considerations

An alternative explanation is suggested by the magnitude of the low temperature maximum of the susceptibility data (χ) which corresponds to a net value of approximately one Ni²⁺ ion per formula unit of BaNi₃(OH)₃(VO₄)₂. A ferrimagnetic transition with spin glass type ordering could account for the behavior observed here where “chains” of Ni²⁺ ions running along one side of the triangles couple to the Ni²⁺ ion residing at the remaining corner of the triangle. Ferromagnetic coupling within these chains offset by antiferromagnetic exchange between the chains and the remaining Ni²⁺ ions would yield ferrimagnetism. The slight curvature observed in the high temperature inverse susceptibility may support this theory. Magnetization, heat capacity and neutron diffraction experiments are in progress to assess the validity of such a model.

Table S1.1. Crystal data and structure refinement for H₄Ba₂Ni₆O₂₀V₄

| | |
|--------------------------------|--|
| Empirical formula | H ₄ Ba ₂ Ni ₆ O ₂₀ V ₄ |
| Formula weight | 577.36 |
| Temperature | 22 °C |
| Wavelength | 1.54060 Å |
| Crystal system | Monoclinic |
| Space group | C2/m |
| Unit cell dimensions | $a = 10.2129 (62) \text{ \AA}$ $b = 5.8155 (35) \text{ \AA}$ $c = 7.8882 (40) \text{ \AA}$ |
| Volume | 564.33(15) Å ³ |
| Z | 2 |
| Density (calculated) | 4.594 mg/m ³ |
| F(000) | 536 |
| θ range for data collection | 10 to 40° |
| Reflections collected | 155 |
| Independent reflections | 147 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 147 / 1 / 23 |
| Goodness-of-fit on F^2 | 3.662 |
| Final R indices [I > 2σ(I)] | R1 = 0.1306, |
| R indices (all data) | R1 = 0.1325, wR2 = 0.3360 |

^a GOF = $(\sum w(F_o^2 - F_c^2)^2 / (n - p))^{1/2}$ where n is the number of data and p is the number of parameters refined. ^b R1 = $\sum ||F_o - |F_c|| / \sum |F_o|$. ^c wR2 = $(\sum (w(F_o^2 - F_c^2)^2) / \sum (w(F_o^2)^2))^{1/2}$.

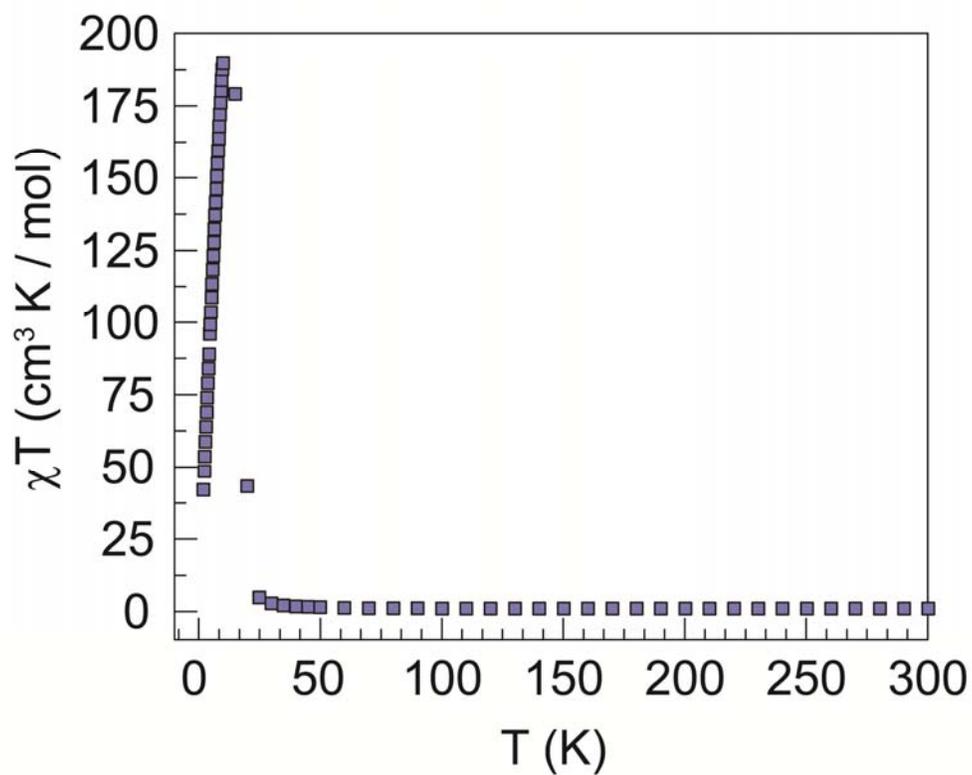


Figure S1. Magnetic susceptibility acquired with an applied dc field of 20 Oe. The linear data correspond to 1 cm³K/mol per Ni ion.