Non-magnetic-ion substitution in geometrically frustrated systems M2(OD)3X[M=Co,Fe,Ni,Mn; X=Cl,Br]

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Geometrically frustrated magnetic materials show novel magnetic properties because of their lattice geometry. The lattice geometries responsible for frustration are generally triangular lattice, kagome lattice, and pyrochlore lattice. Of particular recent interest are the rare-earth pyrochlore compound materials, in which the magnetic ions form networks of corner-shared tetrahedrons and the frustration of spin?spin interactions engenders spin ice states, unconventional spin glass states, and exotic spin liquid states.

In recent years, we identified unconventional magnetic transitions in a transition metal hydroxyhalogenide series of deformed pyrochlore compounds M2(OH)3X, where M represents a d-electron transition metal magnetic ion such as Cu+2, Ni+2, Co+2, Fe+2, and Mnˆ+2ˆ, and X represents halogen ions of Cl-1, Br-1, or I-1. Much of these metal hydroxyhalogenides were found originally in natural minerals. This material category presents a complete series for spins S=1/2 to S=5/2. In particular, clinoatacamite, Cu2(OH)3Cl, showed unconventional magnetic transitions at TN1 = 18.1 K with a very small entropy release, TN2 = 6.4 K and TN3 = 6.2 K, with co-existing order and spin fluctuation. The nature of the TN1 = 18.1 K phase remains largely unknown and attracts much interest. Furthermore, it is the first example of the S = 1/2 Heisenberg quantum spin on a pyrochlore lattice and the parent compound for the substituted " perfect kagome lattice " of herbertsmithite ZnCu3Cl2(OH)6, which exhibits spin liquid behavior.

The pyrochlore compounds M2(OH)3X can be viewed as alternatively stacked layers of As kagome lattice planes and triangular lattice planes consisted by the magnetic ions. As is demonstrated in herbertsmithite ZnCu3Cl2(OH)6, substitution of the magnetic ions on the triangular lattice planes by nbonmagnetic Zn etc. can artificially produce a new kagome lattice for the magnetic ions. We have thus tried such nonmagnetic substitution in the Co2Cl(OH)3 system. We observed by magnetic susceptibility measurements that partial substitution of magnetic Co by nonmagnetic Zn drastically reduced the magnetic transition temperature. With a substitution ratio near 25% in Co3ZnCl2(OH)6 no sharp transition was seen from the magnetization data.

Therefore, we performed neutron powder diffraction experiments using samples of (Co1-xZnx)2Cl(OH)3 with x ranging from 0 to 0.4. The experiments were performed, respectively, with a wavelength of 1.8264 A using a Kinken powder diffractometer, HERMES, of the Institute for Materials Research (IMR), Tohoku University, installed at the JRR-3M reactor at the Japan Atomic Energy Research Institute (JAERI), Tokai. The collected neutron data were refined using the program Fullprof suite based on Rietveld refinement. We found that selective substitution of the Co ions on the triangular lattice planes was realized in the (Co1-xZnx)2Cl(OH)3. For x near 0.25, a kagome lattice of S=3/2 Co was realized. No magnetic transition was seen until the experimentally reachable 1.5 K, suggesting the enhanced frustration and possible spin liquid state in kagome lattice Co3ZnCl2(OH)6.
Data analysis is still in progress and the detailed results will appear in a submitted paper to a physics journal.