ESRF	**Experiment title:** Resonant x-ray scattering on herbertsmithite and Zn-paracatamite crystals	**Experiment number:** HE3063
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Names and affiliations of applicants (* indicates experimentalists):

J.S. Helton*, A. Prodi*, Y.S. Lee.
Department of Physics
Massachusetts Institute of Technology
Cambridge, MA 02139, USA

Report:

The Zn-paratacamite mineral family, $Zn_xCu_{4-x}(OH)_6Cl_2$ features kagome lattice planes of spin-1/2 Cu^{2+} ions, separated by triangular planes occupied by either Cu ions or nonmagnetic Zn ions. The mineral herbertsmithite, $ZnCu_3(OH)_6Cl_2$, appears to be a structurally perfect spin-$\frac{1}{2}$ Cu^{2+} kagome lattice antiferromagnet. Such a system has long been a system of considerable interest in the field of frustrated magnetism. One well known proposal for the ground state of this system is a Valence Bond Solid (VBS) state. The VBS ground state consists of dimer singlet pairs covering the lattice. Some of the most well known calculations supporting the presence of such a VBS state[1, 2] suggest that the most energetically favorable VBS ground state would feature a dimer arrangement pattern that repeats with a unit cell a factor of 12 larger than the structural unit cell. In a variety of other materials, a VBS state has led to subtle structural distortions. Thus such a ground state would lead to a superlattice structure with a large unit cell. Paratacamite minerals with $x \leq 0.6$, the system will undergo a transition to antiferromagnetic Néel order. The goal of the experiment was twofold: 1) investigate in herbertsmithite possible macroscopic structural distortion at low temperature and/or weak superstructure from proposed Valence Bond Solid (VBS) dimerized ground state; 2) elucidate details of the ordered magnetic structure in $Zn_{0.34}Cu_{3.66}(OH)_6Cl_2$ paracatamite crystals which cannot be resolved from powder neutron scattering.

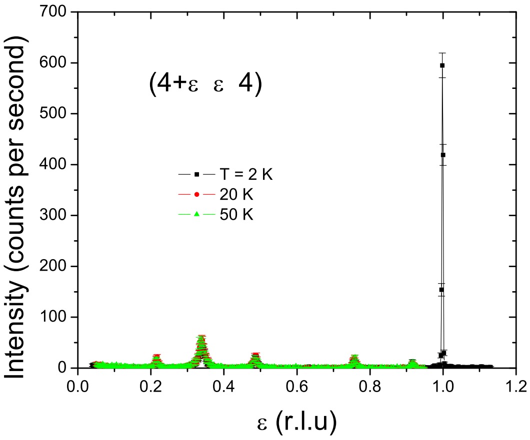

Figure 1: (Scan between the (4 0 4) and (5 1 4) peaks displays only powder rings - no sign of superlattice peaks.

A small single crystal of herbertsmithite was mounted in reflection geometry with the (1 0 1) reflection direction roughly perpendicular to the mount. The sample was cooled to a temperature of roughly 2 K. A scan was launched measuring scattering along the line connecting the (4 0 4) and (5 1 4) reflections. A VBS with an enlargement of that proposed[1, 2] would result in five superlattice reflections along this line. Further, a mesh scan in H and K was performed measuring scattering over more than half of the planar Brillouin zone around this line. This mesh area is sufficient that any symmetric superlattice peak would have been present in this scan region. No superlattice peaks were observed. Fig. 1 shows scans along the line mentioned above at temperatures of 2 K, 20 K, and 50 K. The observed structure is temperature independent and has been confirmed as arising from weak powder peaks. The powder lines are shown along with the very weak (5 1 4) structural peak, and are roughly 250000 times weaker than the primary Bragg refelctions. This places a very low bound on any possible dimerization, and strongly suggests against the presence of a VBS state at a temperature of 2 K. Moreover, peakshape and lattice parameters didn't evidence any symmetry-lowering structural distortion. In summary, we have measured the lattice parameters of herbertsmithite as a function of temperature and confirmed that there are no VBS like superlattice peaks down to 2 K.

The second goal of the experiment was to measure magnetic scattering in $Zn_{0.34}Cu_{3.66}(OH)_6Cl_2$. A sample was likewise mounted in reflection geometry, and we measured scattering in the σ - π polarization channel with the x-ray wavelength tuned near resonance. This measurement was taken as a θ scan through the (-4.5 4 4) position, which was predicted to feature magnetic scattering due to the observed magnetic Bragg peak in neutron powder diffraction[3]. We could not measure magnetic scattering.

References:

[1] P. Nikolic and T. Senhil, Phys. Rev. B **68**, 2144159 (2003).
[2] R.R.P. Singh and D.A. Huse, Phys. Rev. B **76**, 180407 (2007).
[3] S.-H. Lee*, et al.*, Nat. Mat. **6**, 853 (2007).