Experimental report

10/09/2018

Proposal: **4-01-1364** **Council:** 4/2014

Title: 24-spin clusters in the mineral boleite: excitations in spin-liquid droplets?

Research area: Physics

This proposal is a new proposal

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Samples: boleite/K Pb26Ag9Cu24Cl62(OH)48

Instrument	Requested days	Allocated days	From	To
IN4	2	2	15/09/2014	17/09/2014
IN8 Flatcone	4	4	18/09/2014	22/09/2014

Abstract:

The crystal structure of the mineral boleite contains Cu2+ ions (each with S=1/2) forming truncated cube clusters of linked triangles. Susceptibility, neutron scattering and exact diagonalization calculations suggest that effective S=1/2 degrees of freedom emerge on the triangles, followed by condensation of these into a singlet state at lower temperature. We hypothesize that the resulting cube of effective S=1/2 degrees of freedom is a fragment of the full S=1/2 dimer problem on the cubic lattice, where a spin liquid groundstate exists. The clusters in boleite afford an intermediate situation, accessible to both experiment and exact diagonalization, in which a spin liquid "droplet" can be studied. Here we propose to locate and characterize the expected excitations of individual triangles, and to search for low energy excitations associated with the cooperative singlet state.

24-spin clusters in the mineral Boleite: correlations in spin-liquid droplets?
IN4 and IN8, September 2014

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Unconventional ground states and excitations, combined with the possibility of direct connection with quantum many body theories, drive the study of low dimensional, frustrated, magnetic materials with $S = 1/2$ magnetic moments [1]. Boleite ($KPb_{26}Ag_9Cu_{24}Cl_{62}(OH)_{48}$) has so far only been studied crystallographically at room temperature [2, 3]. We here report the preliminary findings of the inelastic neutron studies performed at IN4 and IN8 at ILL on 2.2 g of the mineral Boleite.

An interesting possibility in frustrated magnets is the formation of composite degrees of freedom from small clusters of spins. For example, in $La_3Cu_2VO_9$ [4], strongly coupled clusters of four triangles of $S = 1/2$ are thought to form effective $S = 1/2$ degrees of freedom, which in turn begin to interact, and may then form a spin liquid at low temperature. The mineral Boleite ($KPb_{26}Ag_9Cu_{24}Cl_{62}(OH)_{48}$) contains highly frustrated 24-atom clusters of Cu^{2+} ions as shown in figure 1. The triangles are formed by oxygen mediated bond with an angle of 125.15°. Between the triangles are side bond also formed by oxygen bridges with an angle of 94.65°. This is shown in figure 1.

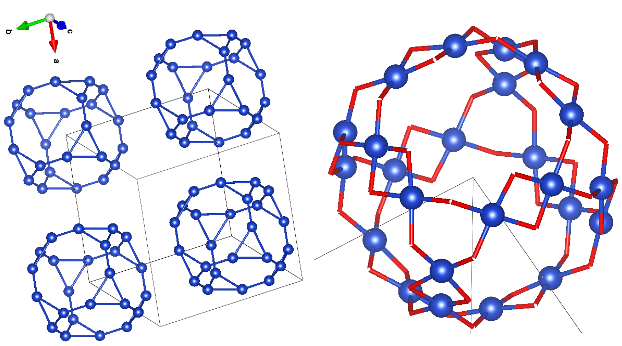

Figure 1: **Left:** A simple illustration of four Copper clusters leaving out all other atoms in the unit cell. **Right:** One Copper cluster with 24 atoms drawn with the mediating oxygen bonds.

We performed two inelastic experiments, at IN4 and IN8, on the same sample of Boleite. The 7 crystals were co-aligned and mounted on an Al holder without use of glue in the (h h k) plane, as shown in figure 2. The system is cubic with a lattice parameter of a=15.128 Å at 2 K.

The over all plan for the two inelastic experiments is to find the signal from the excitations of the triangles in the clusters. The energy transfer has been calculated from a simple six spin model fitted to susceptibility measurements to be 25 meV. The IN4 data should be used to identify the exact energy transfer to use at the IN8 Flatcone experiment.

The IN4 experiment

At the IN4 experiment, an incoming wavelength of 1.27 Å was used for the main data acquisition. The choppers were running with ?? Hz, giving an energy resolution of the elastic line at ?? meV. To obtain a powder average of the co-aligned crystals, we rotated the sample in steps of 2 degrees during the data acquisition. We took data in an Orange cryostat at 1.5 K and 250 K.

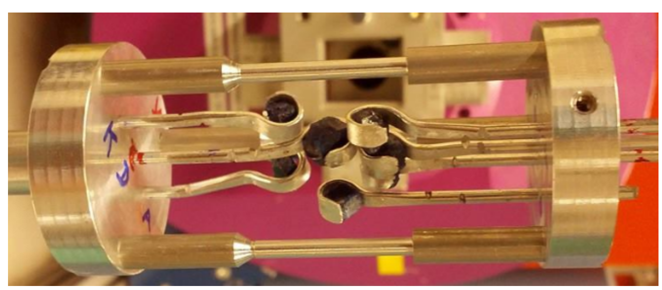

Figure 2: Photo of the co-aligned samples on the aluminum holder with a total mass of 2182 mg.

The main data from IN4 at 1.5 K and 250 K is shown in fig. 3 and 4. At both temperatures, we see very strong featureless scattering, increasing towards high q-values and with temperature. This is most likely phonon scattering, enhanced by inelastic incoherent scattering from the large amount of hydrogen in the unit cell. A minor amount of inelastic scattering is present at low q-values, at energy transfers around 26 meV.

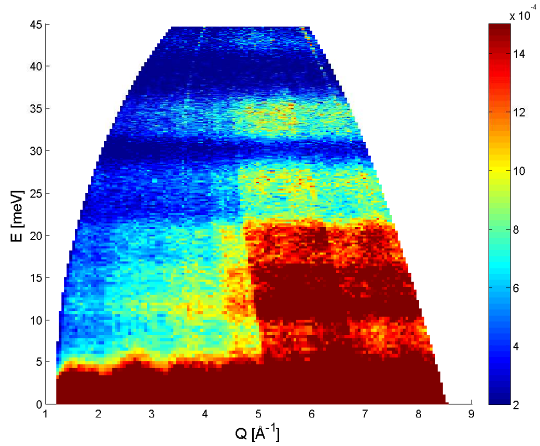

Figure 3: Color plot of the inelastic scattering at 2 K averaged over q by turning the single crystal sample during the data acquisition.

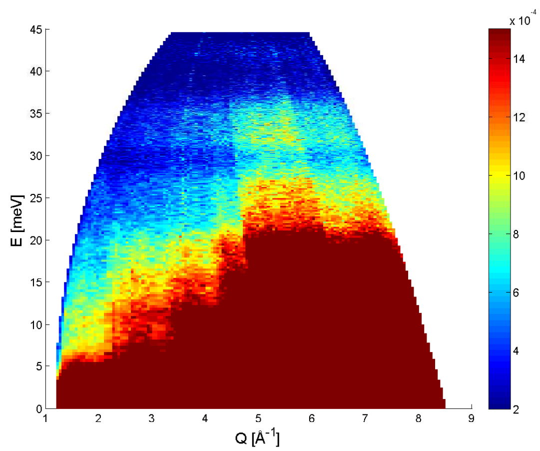

Figure 4: Color plot of the inelastic scattering at 250 K averaged over q by turning the single crystal sample during the data acquisition.

To zoom in on that feature, we show a cut through the data in figure 5 for the two temperatures. Both the temperature and the q-dependence of this signal may suggest that this is not related to phonon scattering. In addition, the energy position of 26 meV is very close to the value of the interaction constant (25 meV) between the elementary triangles. We therefore interpret the inelastic signal as being the breaking of the singlet bonds in the triangles.

In conclusion we will use an energy transfer of 26 meV at the IN8 experiment.

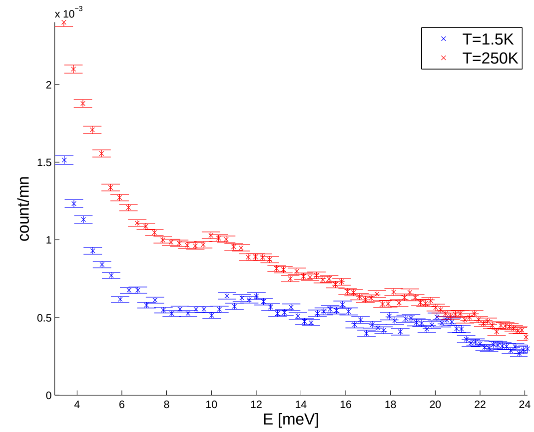

Figure 5: A cut at $q = 1.9 \pm 0.2$ Å^{-1} through the data taken at 2 K and at 250 K.

The IN8 experiment

IN8 was configured in the Flat-cone mode with fixed $k_f = 3.0$ Å^{-1}, or 18.5 meV. Scans consisted of rotating the sample by 120 degrees in steps of 0.5 degrees for the elastic measurement and 1.5 degrees for the inelastic measurements. We typically combined scans with 2 A4 interlayering settings for better coverage in reciprocal space (5 settings for elastic scans). For most scans, we used Si(111) monochromators to avoid second order contamination. A few scans were taken with the PG(002) monochromator, showing serious contamination for nominal energy transfers below 25 meV.
The 7-crystal co-aligned sample was placed in an Orange cryostat. We measured elastic scans, and different energy transfers in the range 20-30 meV, at the base temperature of 1.5 K and at 250 K for background subtraction. The result of the elastic scan is shown in fig. 6. All Bragg peaks are clearly visible. In addition, a peak at a seemingly half-integer position is seen at (1/2 1/2 2). Nowhere else in reciprocal shows a half-integer reflection, and the significance of this is doubtful.
A typical inelastic scan (26 meV energy transfer) is shown in fig 7. The data clearly contains several spurion which we have removed (see fig. 8.
Fig. 9 shows an A3 integration of the scattering. The large-q behavior is typical for a phonon signal.
In conclusion we will have to make a more profound data analysis in order to interpret the data obtained at IN8.

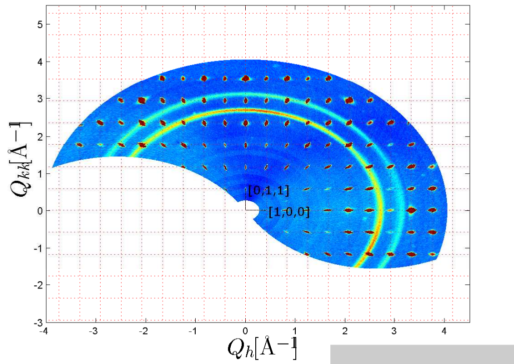

Figure 6: Elastic q map in the (hhk) plane measured at 2 K. The color scale is logarithmic to enhance small features.

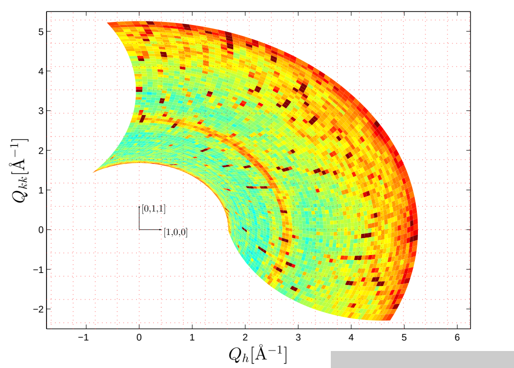

Figure 7: A typical inelastic scan at 26 meV energy transfer. The localized high intensity points (spurions) originates from incoherent or diffuse scattering, of Bragg peaks from the sample, hitting the analyzers.

The IN3 experiment

The peak at q=(1/2 1/2 2) observed at IN8 could not be found again at IN3 in any of the equivalent q positions and we hence conclude that the IN8 signal is of spurious nature.

[1] B. Normand et al., Cont. Phys. **50**, 533 (2009)

[2] R. C. Rouse, Journ. of Solid State Chem. **6**, 86-92 (1973)

[3] M. Cooper et al., CA Mineralogist **38**, 801 (2000)

[4] J. Robert, *et. al*, Phys. Rev. B **77**, 054421 (2008)

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Instrument: IN4 and IN8

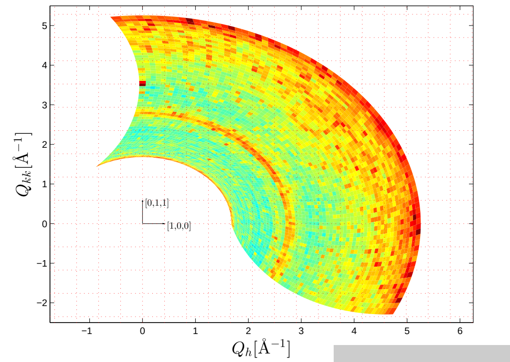

Figure 8: A typical inelastic scan at 26 meV energy transfer with our spurion subtraction.

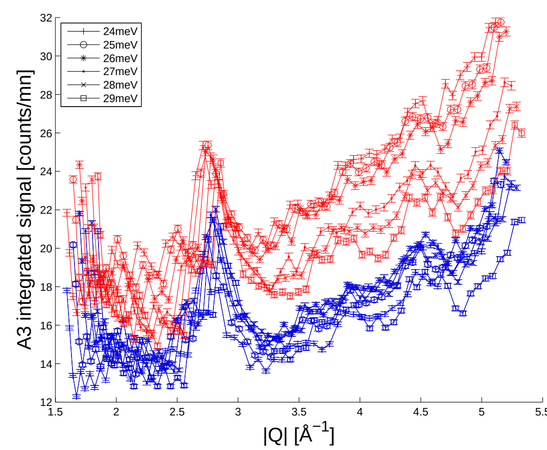

Figure 9: Plot of q dependence of the a3-integrated scattering. Blue colour represents 1.5K. Red colour represents 150K