Experimental Report

21/01/2014

Proposal: **4-04-462** **Council:** 4/2012

Title: Excitations in a geometrically frustrated molecular magnet in a field: Mapping the wavefunctions across the avoided crossing.

This proposal is a new proposal

Research Area: Physics

Main proposer: **OCHSENBEIN Stefan**

Experimental Team: OCHSENBEIN Stefan

Local Contact: MUTKA Hannu

Samples: Na12[Sb2W18Cu3O66(H2O)3].46H2O

Instrument	Req. Days	All. Days	From	To
IN5	7	5	22/05/2013	27/05/2013

Abstract:

Especially tantalizing molecular magnets are triangular antiferromagnetic (AFM) clusters, as they constitute the most basic geometrically frustrated magnet. We plan to do inelastic neutron scattering experiments on aligned single crystals containing an antiferromagnetic Cu(II) triangle to directly determine the tunnel splitting in a magnetic field. This tunnel splitting arises from a combination of Dzyaloshinkii-Moriya interactions and unequal exchange interactions in the presence of a magnetic field in the plane of the triangles.The proposed experiments will allow directly measuring the tunnel splitting at an avoided level crossing, as well as determining the wavefunctions of the involved states, resolving remaining questions concerning the spin Hamiltonian of this material.

Excitations in a geometrically frustrated molecular magnet in a field: Mapping the wavefunctions across the avoided crossing

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Introduction

Frustration effects in magnetism have attracted substantial interest in recent years.[1, 2] The most basic geometrically frustrated magnetic system is an antiferromagnetic triangle.[3] In this experiment we studied the compound $Na_{12}[Sb_2W_{18}Cu_3O_{66}(H_2O)_3]\cdot 46H_2O$ (**1**), which consists of isolated molecules with a Cu(II) triangle (Cu_3 from hereon, Fig. 1a).[4] Divalent copper has a single unpaired electron, and thus a spin s_i =1/2. In an equilateral triangle of spins s_i = 1/2 the antiferromagnetic exchange interactions lead to a degenerate ground state of two doublets and an excited quartet state. In Cu_3 the Cu(II)-spins are coupled antiferromagnetically, but the combined effects of non-equal exchange interactions ($J_{12} = J_{13} \neq J_{23}$, isosceles triangle) and Dzyaloshinskii-Moriya (DM) interactions relieve some of the frustration, resulting in a splitting between the two ground doublets (a schematic energy level diagram is shown in Fig. 1b). In order to improve the understanding of these interactions, especially the DM interactions, we attempted to measure the exchange and Zeeman splitting of the relevant states using inelastic neutron scattering (INS) spectroscopy of **1** in a magnetic field applied parallel to the triangle plane.

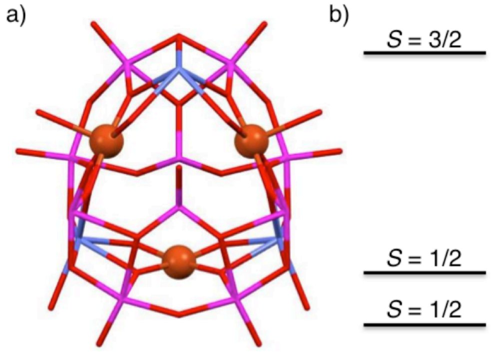

Figure 1. a) Molecular structure of Cu_3. Cu: orange balls, O: red, W: purple, Na: blue. b) Schematic energy level diagram for an isosceles s_i = 1/2 antiferromagnetic triangle.

Experimental

Deuterated single crystals of **1** were synthesised following literature procedures,[4] but replacing H_2O with D_2O. Several plate-like crystals (total mass ~0.6 g) were grown by slow evaporation of the reaction solvent, D_2O.

INS experiments were done on the time-of-flight spectrometer IN5, equipped with a dilution refrigerator and a vertical field magnet. The crystals were attached to the floor of a copper cylinder, such that the crystal *b*-axis is parallel to the magnetic field, ensuring that the magnetic field lies in the plane of the triangles. Experiments were performed at a temperature of 55 mK with initial neutron wavelengths λ_i of 5.0 and 6.5 Å in magnetic fields between 0 and 2.5 T.

Results and discussion

Figure 2a shows the INS spectra recorded on IN5 with λ_i = 6.5 Å at 55 mK between 0 and 2.5 T in steps of 0.5 T. At zero field peaks are seen at ~0.6 and ~0.8 meV in addition to the strong elastic line. With increasing field the peak at ~0.6 meV splits into three components, one of which stays at ~0.6 meV, one moves higher in energy and one lower, as indicated by the solid lines in Fig. 2a. The peak at ~0.8 meV is not affected by the magnetic field, and is thus most probably a spurious peak. At 1.5 T a shoulder appears on the elastic line, which moves to higher energy with increasing field. In order to quantify the peak parameters Gaussian fits were applied to the spectra. The resulting peak positions are shown as open squares in Fig. 2b. The solid lines in Fig. 2b were calculated using the spin Hamiltonian, eq. 1, and parameters from ref. 5:

$$\mathscr{H} = -2\sum_{i\neq j}\sum_{\alpha=x,y,z} J_{ij}^{\alpha}\mathbf{s}_i\mathbf{s}_j + \sum_{i\neq j}\mathbf{D}_{ij}\cdot\left[\mathbf{s}_i\times\mathbf{s}_j\right] + \mu_B\sum_i \mathbf{g}_{ii}\mathbf{s}_i\mathbf{H}\,, \qquad (1)$$

where $\mathbf{s}_i$ is the spin vector of the i^{th} Cu(II) ion, J_{ij}^{α} are the exchange coupling constants, $\mathbf{D}_{ij}$ the DM vectors, $\mathbf{g}_{ii}$ the g-tensors, $\mathbf{H}$ the magnetic field vector, and μ_B the Bohr magneton.

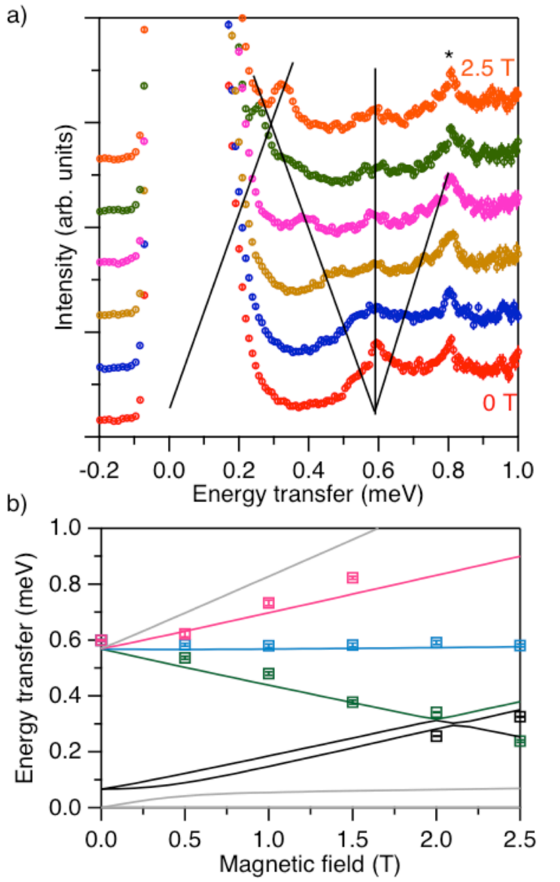

Figure 2. a) INS spectra obtaine with λ_i = 6.5 Å at 55 mK between 0 and 2.5 T in steps of 0.5 T. Solid lines are guides to the eye. b) Extracted peak positions (☐) from spectra with Gaussian fits, and calculated energies based on ref 5.

From Fig. 2b it becomes clear what type of transitions are observed, and the involved states can be labelled by the dominant contribution $|S\ M_S\rangle$ to their wavefunction. At zero-field the ground state consists of one of the two $|1/2\ M_S\rangle$ states, and an excitation to the $|3/2\ M_S\rangle$ state is observed. In a magnetic field these states split into their M_S components, such that the ground state becomes $|1/2\ -1/2\rangle$, and excitations are observed to the $|3/2\ -3/2\rangle$, $|3/2\ -1/2\rangle$, and $|3/2\ +1/2\rangle$ states. The strong transition appearing at fields of ≥1.5 T corresponds to an excitation from the $|1/2\ -1/2\rangle$ ground state to the $|1/2\ +1/2\rangle$ excited state, originating from the same doublet.

The agreement between calculation and experiment is quite good, considering that there were no adjustable parameters. However, calculating the INS spectra reveals that the observed intensities don't match up very well, and that further work is needed refining the model, which should yield detailed insights into the interactions governing the magnetic properties of this frustrated magnet.

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[2] I. Mirebeau and S. Petit, J. Magn. Magn. Mater. **350**, 209 (2014).
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