Experimental report

21/09/2016

Proposal: 5-41-895 **Council:** 4/2016

Title: Magnetic structure of copper guanidinium formate: noncollinear magnetism as a route to spontaneous magnon decay?

Research area: Physics

This proposal is a new proposal

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Samples: CuGF

Instrument	Requested days	Allocated days	From	To
D9	4	5	06/09/2016	11/09/2016
D3 CPA	5	5	30/08/2016	04/09/2016

Abstract:

The multiferroic metal-organic perovskite copper guanidinium formate is structurally analogous to KCuF3, and like its inorganic counterpart is a good realisation of the S=1/2 1D Heisenberg antiferromagnet. In this material, however, our previous work (LET, ISIS) has demonstrated that even in the 3D ordered phase there are no well-defined spin-waves. Instead, there is a clear excitation continuum, suggesting that spontaneous magnon decay plays an important role in this system's dynamics. Theoretical research has shown that such a decay of spin-waves can arise if the magnetic structure is noncollinear. Therefore, to complete our study on this material, we propose to measure the magnetic structure of CuGF. Due to symmetry constraints, this requires the use of polarised neutrons: this proposal calls for both unpolarised time on D9, to determine the nuclear structure in detail, and polarised measurements using Cryopad on D3. As well as being a potential example of non-collinearity shortening magnetic lifetimes, the data obtained will help to elucidate complex magnetic behaviour in functional MOFs and the ways in which their magnetic properties differ from their inorganic analogues.

Preliminary experimental report

Polarimetry (D3 + CRYOPAD)

We mounted three samples in the (*hk*0), (0*kl*), and (*hhl*) scattering planes and collected full polarisation matrices from a selection of diffraction peaks.

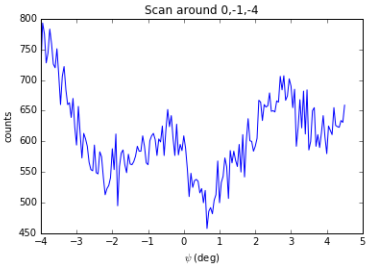
The major problem we encountered with this experiment was that the relatively large crystals needed for good signal gave strong multiple scattering, of similar intensity to the weak magnetic contributions. As a result, peaks that are forbidden by the $Pna2_1$ space group symmetry had substantial intensity even above the Néel temperature, making it very difficult to isolate the magnetic contribution to these peaks. For instance, the apparent polarisation P_{xx} of the "pure magnetic" peak (001) at 2 K was 0.27. We attempted to correct for this by subtracting the equivalent measurement at 10 K from each channel. Assuming an analyser efficiency of 85% (based on measurements of purely structural peaks) this gave a more realistic $P_{xx}(001) = -0.98$. However, the full polarisation matrix based on the same analysis is

$$P(001) = \begin{pmatrix} -0.98 & -0.10 & -0.02 \\ 0.34 & -0.22 & -0.04 \\ -0.07 & -0.09 & 1.08 \end{pmatrix}$$

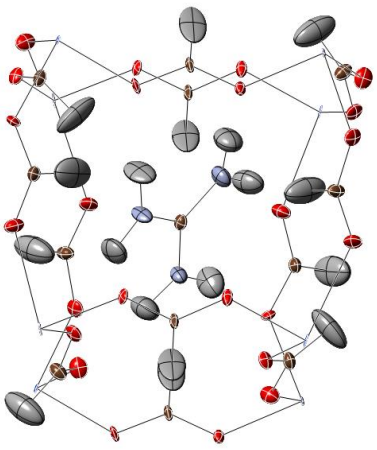
in which the *y* row appears impossible. The results from different peaks were similarly difficult to interpret, and it will take substantial further work to extract meaningful results from them.

Unpolarised diffraction (D9)

This experiment was performed entirely on the final sample from D3, mounted in the (*hhl*) scattering plane (although of course this detail is less relevant to a four-circle goniometer experiment).



We confirmed that the intensity of forbidden reflections was due to multiple scattering by performing several ψ-scans, which showed substantial variation in intensity over small changes in angle (right).



We obtained a good single-crystal data set at 10 K and were able to refine the nuclear structure against these data ($wR2 = 0.0794$, 1092 data, 210 parameters; right). This model also included refinement of the deuteration fraction at the two chemically distinct sites, showing that the formate site is entirely deuterated within experimental error whereas the guanidinium site has 16.0(5)% ^{1}H, or roughly one proton per unit cell. This is an encouraging result as it may help to explain the magnon decay we are investigating, since disruption to the hydrogen bonding between guanidinium and formate ions is likely to result in a form of magnetic bond doping. Even small amounts of such doping, in this case Br/Cl substitution, in piperazinium hexachlorodicuprate (PHCC) reduce the magnon lifetime in that material [1].

Again, however, the multiple scattering made it very difficult to measure a convincing magnetic structure. In much the same way as on D9, we attempted to do this by taking a series of very long (2 hours per peak) measurements both above and below the Néel temperature (10 K and 2 K respectively). However, the difference data set did not allow a viable magnetic refinement.

For this reason the next steps in this project are likely to involve remeasuring at longer wavelength in an attempt to reduce the contribution of multiple scattering.

Anthony Phillips
21 September 2016

Reference

[1] D. Hüvonen *et al.*, *Phys. Rev. B* **86**, 214408 (2012).