Experimental Report

26/11/2013

Proposal:	**4-04-463**	**Council:**	4/2012
Title:	Polarised inelastic neutron scattering of a cobalt(II) cubane single-molecule magnet		

This proposal is a new proposal

Researh Area: Physics

Main proposer: **MURRIE Mark**

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Samples: [C(ND2)3]8[Co4(C6D7O7)4]·4D2O

Instrument	Req. Days	All. Days	From	To
D7 He3 Spin Filter	16	16	23/11/2012	09/12/2012

Abstract:

We propose polarized INS experiments to determine the exchange splitting in the SMM (C(NH2)3)8[Co4(cit)4]. Co4 has a cubane-type structure, with the Co(II) ions bridged by oxo-atoms from the citrate ligands. Bulk magnetic measurements indicated predominant ferromagnetic interactions between the Co(II) spins, and from ac magnetic susceptibility measurements an energy barrier for reversal of the magnetization of ~14.5 cm-1 could be determined. INS measurements with 3.2 Å on FOCUS (SINQ, Switzerland) revealed strong phonon scattering below 6 meV, obfuscating the magnetic excitations expected in this energy range (two small peaks at ~1.5 and ~2.4 meV are possibly magnetic excitations). We propose to do polarized INS experiments on D7, as such experiments would allow differentiating between magnetic and non-magnetic scattering. To the best of our knowledge, these experiments would be the first polarized INS experiments on an SMM, and D7 is the only instrument that makes such an experiment possible, thanks to the high neutron flux and the multidetector setup.

Polarised inelastic neutron scattering of a cobalt(II) cubane single-molecule magnet

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Introduction

The aim of this experiment was to determine the exchange interactions in a Co(II) cubane single molecule magnet (SMM) using inelastic neutron scattering (INS) spectroscopy. SMMs are molecules, mostly transition metal clusters, characterised by slow relaxation of the magnetisation. The origin of this slow relaxation is poorly understood in Co(II) containing SMMs, because of the non-zero orbital angular momentum of the Co(II) $^4T_{1g}$ electronic ground state. The magnetic properties of Co(II) clusters are determined by spin-orbit coupling, (low-symmetry) ligand-field interactions, and the exchange interactions between the Co(II) ions. At low temperatures, the problem can be simplified using a model with anisotropic exchange interactions between effective spins, $s' = ½$. INS allows directly measuring the energy splitting governed by these anisotropic exchange interactions, which gives insights into the origin of the slow relaxation of the magnetisation of such Co(II) SMMs. Initial INS experiments on the title compound with unpolarised neutrons on FOCUS (PSI, Switzerland) were marred by what appeared to be phonon scattering. Polarised neutron scattering experiments on D7 (ILL) were therefore envisioned as a way to separate magnetic and nuclear scattering.

We observed several magnetic excitations in our D7 experiment, and are currently finalising the model that allows us to describe the origin of the slow relaxation of the magnetisation of this Co(II) cubane SMM. Additional polarised diffraction experiments on D7 contained information on the different contributions to the total scattering intensity.

Experimental

Polarised neutron scattering experiments were performed on a 4.45 g powder sample of the SMM $[C(ND_2)_3]_8[Co_4(cit\text{-}d_4)_4]\cdot 4D_2O$ (Co_4cit)[1] on the diffuse scattering spectrometer D7 at the Institut Laue-Langevin (ILL). An incident neutron wavelength of λ_i = 3.12 Å was selected with a pyrolytic graphite monochromator. Empty can, quartz, and vanadium measurements were used to correct for the background, and to assess polarisation and detector efficiencies.

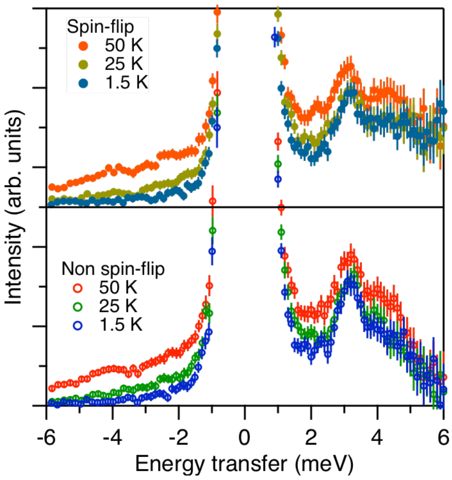

Figure 1. INS spectra of Co_4cit measured on D7 with λ_i = 3.12 Å.

Results and discussion

Excitations. For the inelastic neutron scattering (INS) experiments a Fermi chopper was moved into the beam before the sample position, transforming D7 into a time-of-flight (TOF) spectrometer. In the TOF mode only z-polarisation analysis is possible, differentiating non-spin-flip (*nsf*) and spin-flip (*sf*) scattered neutrons. Figure 1 contains INS data measured on D7: the spectra recorded at

1.5, 25, and 50 K summed over *Q* are shown, whereby the *sf* channel is offset for clarity. The *nsf* and *sf* spectra contain contributions from nuclear coherent and isotope incoherent (*nuc*), nuclear spin incoherent (*inc*), and magnetic (*magn*) scattering. With only *z*-polarisation analysis a complete decomposition is not possible, but the *magn*, and *nuc* contributions can be separated (see Fig. 2):[2]

$$I_{magn} + 4/3 I_{inc} = 2 I_{sf} \qquad (1a)$$
$$I_{nuc} - 1/3 I_{inc} = I_{nsf} - I_{sf} \qquad (1b)$$

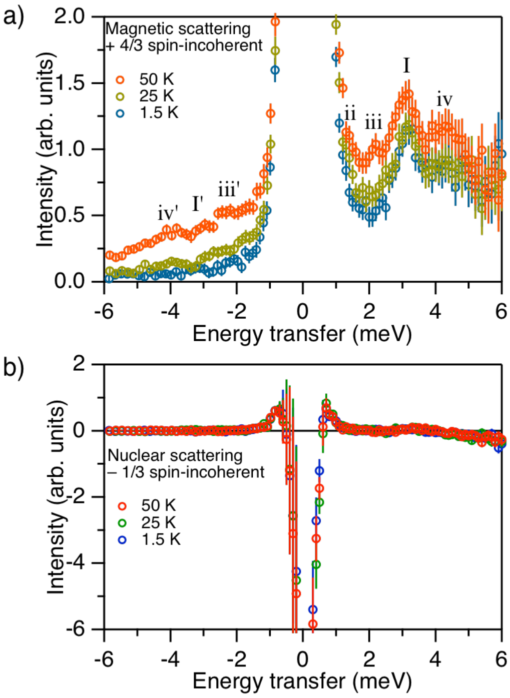

Figure 2. Spectra derived from Fig. 1: a) $I_{magn} + 4/3 I_{inc} = 2 I_{sf}$; b) $I_{nuc} - 1/3 I_{inc} = I_{nsf} - I_{sf}$.

In Fig. 2a several peaks are observed that are attributed to magnetic transitions. Peak I at ~3.2 meV, visible at all three temperatures, is an excitation from the spin ground state of Co_4cit to an excited state (Peak I': respective de-excitation on the neutron energy gain side). Further three peaks (ii: ~1.25 meV, iii: ~2.2 meV, iv: ~4.5 meV) corresponding to transitions between excited states are observed with increasing temperature, as are the counterparts iii' and iv'. These transitions and their temperature dependence allowed us to construct an energy level diagram, which we are in the process of modelling.

From Fig. 2b it is apparent that there are no significant nuclear excitations, i.e. phonons, in the measured energy-transfer range, apart from small quasi-elastic contributions. The elastic peak is dominated by nuclear spin incoherent scattering, as is clear from the negative intensity at ~0 meV. The small negative intensity above ~4 meV seen in Fig. 2b is also a sign of *inc* scattering, indicating that some of the intensity at higher energy seen in Fig. 2a is in fact also *inc* and not *magn*.

Diffraction. For these experiments the chopper was removed, yielding energy-integrated data. Without the chopper polarisation analysis in *x*, *y*, and *z* could be applied, and the three components *nuc*, *inc* and *magn* extracted from the total scattering intensity. Figure 3 shows the 1.5 K scattering intensity as a function of *Q*. The total scattering is dominated by *nuc* and *inc*, whereby *nuc* consists mostly of Bragg peaks. The differential cross section for *inc* scattering can be described by the following equation:[3]

$$\frac{d\sigma}{d\omega} = \sum_i \frac{\sigma_{inc}^i}{4\pi} N_i \exp(-2W), \qquad (2)$$

where σ_{inc}^i is the incoherent neutron scattering cross section of the i^{th} atom in the molecule, N_i is the number of atoms i per molecule, and $\exp(-2W)$ is the Debye-Waller factor (≈1 at low temperatures). With only the extent of deuteration as adjustable parameter, it can easily be determined that for an average $d\sigma/d\omega$ = 145 barns st^{-1} molecule^{-1} the H/D ratio comes out to be approximately 21/51. This result would indicate that the deuteration of the sample was not as complete as expected, or that exchange of D_2O with atmospheric H_2O is possible despite extensive hydrogen bonding in Co_4cit.

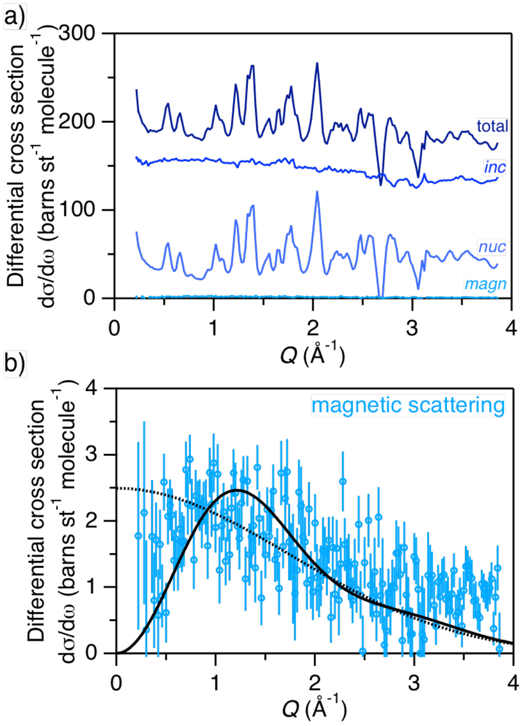

Figure 3. a) Differential neutron scattering cross section vs. *Q*, the individual contributions are shown. b) Magnetic scattering including calculated curves.

The magnetic scattering (Fig. 2b) is weak, and thus noisy. A broad maximum at around 1 Å^{-1} is observed. The dotted line in Fig. 2b is the scaled square of the magnetic form factor *F*(*Q*) for Co(II), while the solid line was calculated using eq. 3,[3] where R = 3.219 Å and R' = 3.171 Å are the Co-Co distances in Co$_4$cit. This equation is a simplification, as in principle the magnetic scattering contains information on the correlation between the Co-spins, but the low intensity and thus substantial noise does not allow a much more detailed analysis.

These results strikingly demonstrate how weak the magnetic contribution to the total scattering in such molecular magnets is, and how astonishing it is that magnetic excitations can routinely be measured. The opportunity to do polarisation analysis to separate magnetic from other scattering may therefore become a useful tool in the study of molecular magnets, and D7 should play a pioneering role in these developments.

$$\frac{d\sigma}{d\omega} \propto F(Q)^2\left(\left(1-\frac{\sin(QR)}{QR}\right)+2\left(1-\frac{\sin(QR')}{QR'}\right)\right), \tag{3}$$

References

[1] K. W. Galloway, A. M. Whyte, W. Wernsdorfer, J. Sanchez-Benitez, K. V. Kamenev, A. Parkin, R. D. Peacock, and M. Murrie, Inorg. Chem. **47**, 7438 (2008).

[2] O. Scharpf and H. Capellmann, Phys Status Solidi A **135**, 359 (1993).

[3] G. L. Squires, *Introduction to the Theory of Neutron Scattering* (Dover Publications, Inc., Mineola, NY, 1978).