Experimental report

20/05/2022

Proposal: **EASY-928** **Council:** 10/2020

Title: Inelastic Neutron Scattering on Cobalt Single Molecule Magnets

Research area: Physics

This proposal is a new proposal

Main proposer: **David HUNGER**

Experimental team:

Local contacts: Bjorn FAK

Samples: (HNEt3)2[Co(bmsab)2]

Instrument	Requested days	Allocated days	From	To
PANTHER	24	24	23/06/2021	24/06/2021

Abstract:

For the characterization of single molecule magnets (SMMs), insight into their magnetic structure is crucial. The magnetic anisotropy of an SMM is determined by the splitting of the electronic ground state due to zero-field splitting (ZFS). For an in-depth characterization, it is necessary to know the magnitude of the ZFS, which can be >>10 meV.
An excellent tool is inelastic neutron scattering (INS). Additionally, a characterization of the phonon states of the SMM is feasible with INS. INS is also superior to EPR spectroscopy, as transitions with $\Delta S=\pm1$ are allowed, a fact that will be crucial for the understanding of the electronic structure of the Co SMM, we are working on. In the current study, we propose to investigate a tetrahedral Co(II) SMM by INS. In far infrared (FIR) spectra at various magnetic fields of the complex, a field dependent feature at 28 meV is found, which can be assigned to the transition between the two zero-field split Kramers doublets of the S=3/2 state. Also, strong signatures of substantial spin-phonon coupling are observed. Here, INS measurements at max. two temperatures may help elucidating the nature of the field dependent features in the FIR-spectra.

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The aim of this experiment was the investigation of the magnetic excitations in a mononuclear cobalt(II) single-molecule magnet (SMM). SMMs are a class of molecular magnetic materials, that show classic magnetic behaviour, such as slow relaxation of the magnetization, but in contrast to long-range ordered ferromagnets, interactions between the various magnetic centres are missing. This fact makes them promising candidates for novel high density data storage applications.

The studied compound in this experiment was a tetrahedral cobalt(II) complex with the chemical formula $(HNEt_3)_2[Co(II)(L^{2-})_2]$ (with H_2L = 1,2-bis(methanesulfonamido)benzene), that was characterized by magnetometry and magnetic-field-dependent far infrared spectroscopy (FIR) before and displays slow relaxation of the magnetization [1]. The compound itself also serves as a building block for a more complex, binuclear cobalt(II) SMM [2]. FIR measurements of $(HNEt_3)_2[Co(II)(L^{2-})_2]$ showed an intense field dependent signal at 230 cm^{-1} (28 meV), fitting the energy gap for magnetization reversal, as it was first determined by magnetometry. Also, substantial spin-phonon interaction was observed in the FIR spectra. Following this, the main aims of this EASY experiment were: 1) Confirmation of the magnetization reversal gap found by magnetometry and FIR. 2) Investigation of the phonon character of this transition. 3) Obtain a first study on the mononuclear compound for future, comparative measurements on the binuclear compound. 4) Test, if non-deuterated samples of such compounds are measurable.

Since the experiment was performed as an EASY proposal, 1500 mg of sample were sent to the ILL. The requested temperatures and energy range were 10 K, 50 K, 100 K and up to 35 meV, respectively. In a first run, all sample was loaded in a vanadium container and data was collected at 1.5 K, 50 K and 100 K with E_i = 50 meV. Measurement time at each temperature was 2 h. In this first series, no magnetic transitions were observed. One problem of the measurements might have been too much sample in the beam, resulting in strong incoherent elastic scattering of the hydrogens in the sample. This can lead to a redistribution of the phonon scatter to smaller wave vectors and to a possible masking of magnetic transitions. To tackle this, a second measurement series was carried out with less sample in the beam path. Measurements were performed in this case again with E_i = 50 meV and at 1.5 K, 50 K and 100 K. In an energy scan at Q = 2.5 $Å^{-1}$ at various temperatures, a decrease of intensity with increasing temperatures of a signal at 32.5 meV is found, hinting towards a magnetic character of this transition (Figure 1).

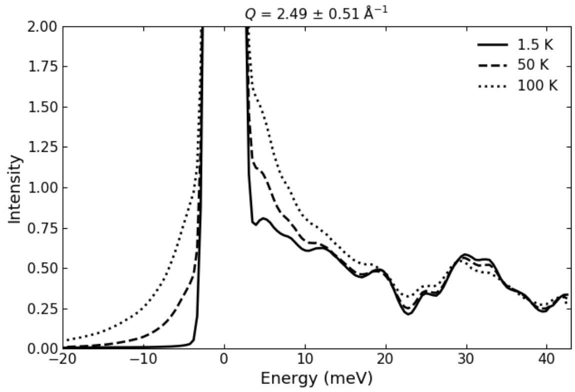

Figure 1: Energy scans at Q = 2.5 $Å^{-1}$ for different temperatures as indicated in the figure. The peak at 32.5 meV is decreasing with increasing temperature, hinting towards partially magnetic character.

In contrast to this, different behaviour is observed when looking at the Q dependence at different energies. For magnetic transitions, decreasing intensity with increasing Q is expected, which is not the case in the measured system (Figure 2).

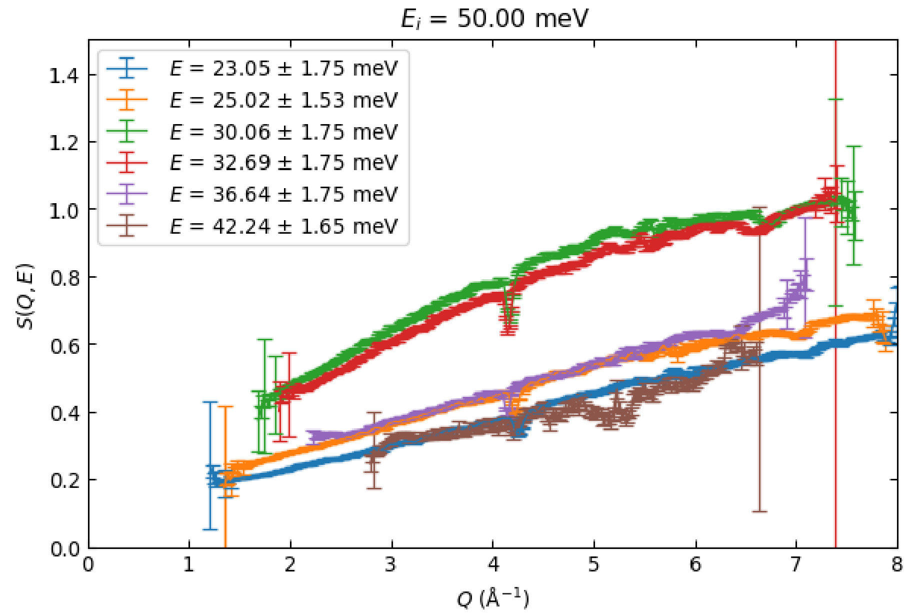

Figure 2: Q scans at different energies at a temperature of 1.5 K. Increasing intensity with increasing Q points towards only phonon character of the various signals.

At high Q values, magnetic scattering is expected to be small due to the decrease of the magnetic form factor and hence no magnetic peaks should be observable. Nevertheless, measurements at Q = 6 Å^{-1} are showing the same temperature dependence of $S(Q, E)$ as at Q = 2.5 Å^{-1}, which is again indicative for only phonon related signals (Figure 3).

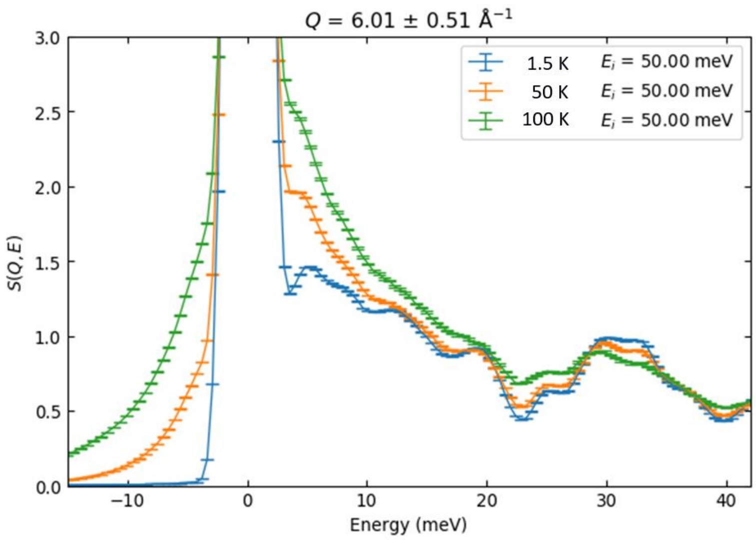

Figure 3: Energy scans at Q = 6 Å^{-1} for the temperatures as indicated in the figure. The same temperature dependence of the signals as in Figure 1 is found, which is indicative, that only phonons are observed.

Interestingly, not all signals feature the same temperature dependence. This gets clear, when the difference of *S*(*Q, E*) of the measurement at 1.5 K and at 50 K is plotted (Figure 4). Here, it is found, that the signal at 32 meV is not showing the same *Q* dependence as the other branches, which might hint again to a partial magnetic character.

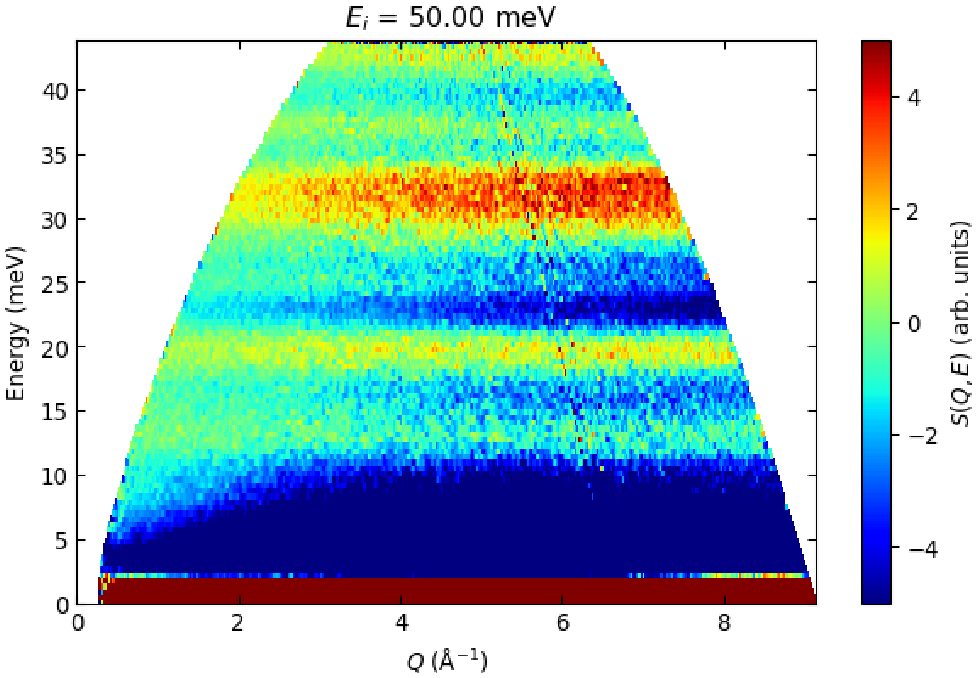

Figure 4: Difference of *S*(*Q,E*) measured at 1.5 K and at 50 K. The branch at 32.5 meV is not showing the same *Q* dependence as the other branches, hinting to an at least partial magnetic character of the signal at that energy.

In conclusion, with this EASY experiment, it was possible to obtain a first idea of the signals that can be expected in such cobalt(II) SMMs, where one key molecule was investigated. No clear indication of signals with mainly magnetic character was found, but an unusual *Q* dependence of different phonon branches was observed.
The measurements carried out in the EASY-928 proposal will serve as comparative measurements in future inelastic neutron scattering experiments on the structurally related dimeric species. Additionally, they serve as a good starting point for future measurements on the same sample. One step further would be tuning the *Q*-range by changing the incoming energy in order to have a better separation of phonons and magnetic transitions.

All measurements were performed by Bjorn Fak, who is greatly acknowledged here for his support.

References:

[1] Y. Rechkemmer, Nat. Commun. **7**, 10467 (2016).
[2] U. Albold, Angew. Chem. Int. Ed. **58**, 9802–9806 (2019).