Experimental report

09/08/2022

Proposal: **4-06-19**

Council: 4/2021

Title: Magnetic excitations in high-Tc metal-organic magnets

Research area: Materials

This proposal is a new proposal

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Samples: Li0.7[Cr(pyrazine)2]Cl0.7*0.25THF
CrCl2(pyz)2
Li0.7[Cr(pyz)2]I0.7*0.25THF, pyz=C4D4N2, THF=(CD2°4O

Instrument	Requested days	Allocated days	From	To
PANTHER	3	2	13/09/2021	15/09/2021

Abstract:

Permanent magnets are essential components in many green energy technologies, e.g. in wind turbines or in motors in electrical vehicles. Metal-organic (MO) magnets, networks of metal ions coordinated to organic ligands which have magnetic properties, have shown promising prospects in the development of the next generation of permanent magnets.

We propose to investigate two similar MO magnets: One which have recently broken the record for both critical temperature and coercivity, as well as a simpler compound from which the first one is derived. Our objective is to determine the exchange couplings within the 2D coordination networks of chromium and pyrazine in these compounds using INS. We also seek to identify or prelude the role of inter-layer coupling and to identify the effect on the spin-orbit coupling caused by the difference in oxidation state between the two compounds (Cr(II) vs. Cr(III)). Our results will guide coordination chemists in their further development of MO magnets for industrial applications.

Experimental Report – 4-06-19

Introduction

In 2020, members of our collaboration published the synthesis and bulk magnetic properties of a layered metal-organic framework $Li_{0.7}Cr(pyrazine)_2Cl_{0.7}\cdot 0.25$ THF **(1)** with a record-breaking critical temperature of 510 K and a giant room-temperature coercivity of 7500 Oe [1]. These properties are caused by extraordinary strong Heisenberg exchange between anisotropic Cr^{II} ions and radical pyrazine within 2D square-planar layers leading to ferrimagnetic order with DFT predicting a coupling constant of $J \approx -50$ meV ($-2J$ convention). The goal of experiment 4-06-19 was to measure the spin dynamics of **(1)** for the first time in order to experimentally determine the exchange couplings within the 2D planes and to identify or preclude the role of inter-layer exchange coupling. Initial modelling using SpinW[2] predicted an intense flat band at ca. 60 meV when assuming J = -50 meV (Fig 1.). Since we did not manage to synthesise a deuterated version of **(1)**, we also performed experiments on a deuterated analogue Li_xCr(d-pyrazine)2$I_x\cdot$Y THF **(2)** which has similar magnetic properties and is expected to have a similar magnetic spectrum (thus far unpublished).

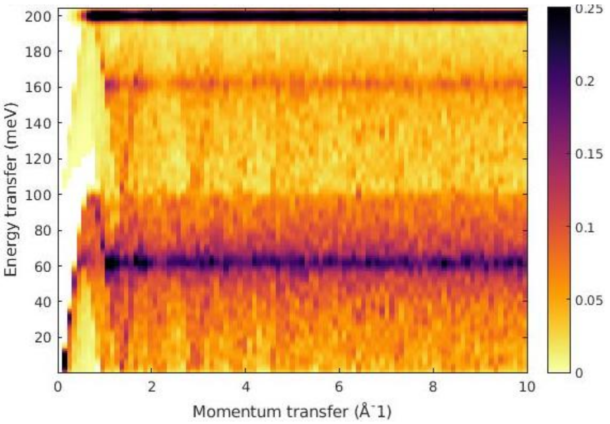

Fig. 1: Simulated S(Q,E)-map calculated with SpinW[2] for a model of **(1)**. Isotropic Cr^{II} ions (S = 2) are coupled (J = -50 meV) to two localised $S = ½$ ions representing the pyrazines in a 2D square-planar lattice. Magnetic form factors were disregarded since the pyrazine form factor was not known.

Results and initial analysis

Spectra of **(1)** and **(2)** were collected using E_i = 19, 76, 112 and 150 meV at T = 1.6 K (all) and 100 K (**(1)**: 19 and 150 meV only, **(2)**: 150 meV only). To highlight an example, the E_i = 76 meV spectra, with a measured empty can signal subtracted, are shown in Fig. 2 (upper row). For **(1)**, two distinct dispersionless excitations were found at ca. 31 and 55 meV, while a big blob of intensity extends from the elastic line around Q = 3 $Å^{-1}$ and merges with the dispersionless band at 31 meV at Q = 6 $Å^{-1}$. This general shape is maintained for **(2)** with the blob now extending all the way to Q = 2 $Å^{-1}$ and the highest-E excitation having moved to slightly lower E ≈ 45 meV. These features all increase in intensity with increasing Q and are therefore assigned as vibrational modes. Thus, no magnetic signal was observed in the raw E_i = 76 meV data for either compound. This was in general true regardless of compound and of E_i, as exemplified from the E_i = 150 meV spectrum of **(1)** (Fig. 2, lower left). The absence of any magnetic signal in the data from **(2)** suggests that lack of deuteration is not the reason for a missing magnetic signal in the data from **(1)**.

Several methods for subtracting scattering from vibrations were tried to extract scattering of magnetic origin. One typical method is to subtract spectra measured at elevated temperatures (here 100 K) from low-T spectra. For us, this did not work for two reasons: 1) The magnetic

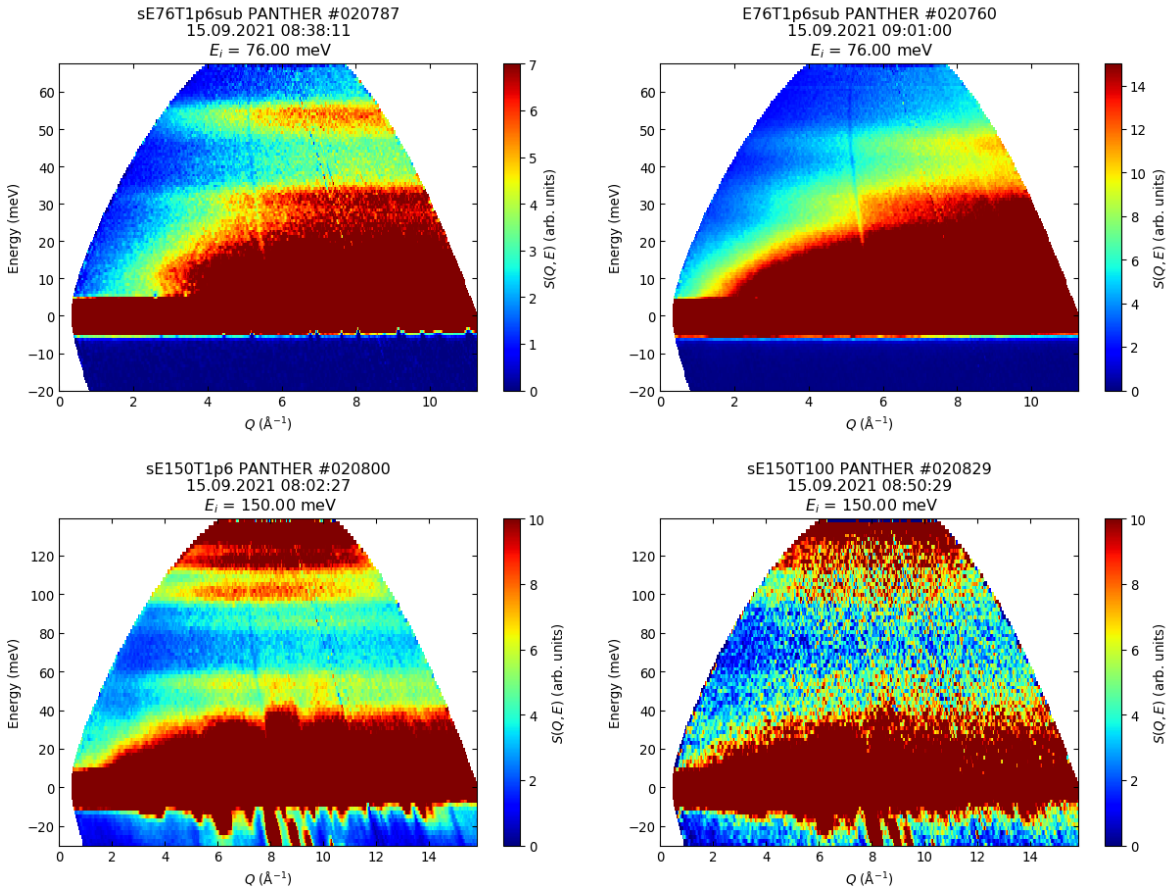

Fig. 2: S(Q,E)-maps measured with PANTHER of **(1)** using E_i = 76 meV at T = 1.6 K (upper left), of **(2)** using E_i = 76 meV at T = 1.6 K (upper right), of **(1)** using E_i = 150 meV at T = 1.6 K (lower left) and at T = 100 K (lower right).

interactions in **(1)** and **(2)** are presumed to be very strong, and magnetic order persist way above room temperature. Therefore, it is difficult to know for certain that any magnetic signal has vanished at the elevated temperature, and one might subtract magnetic intensity in addition to intensity of vibrational origin. 2) The quality of data measured at T = 100 K was quite poor, as exemplified by the T = 100 K, E_i = 150 meV spectrum of **(1)** (Fig. 2, lower right), which made it impossible to extract magnetic scattering by subtraction of spectra measured at higher T.

As an alternative, we tried to extrapolate the full phonon spectrum of **(1)** and **(2)** using only parts of the measured S(Q,E)-maps believed to contain minimal magnetic intensity ($Q > 6$ Å^{-1}). The approach is sketched out in Fig. 3 for the E_i = 76 meV data of **(1)**. First, an integration along the E-axis around a well-defined excitation (here E = (55 ± 5) meV) yields a I(Q) data set. The approximate expression $I(Q) = a + bQ^2e^{-cQ^2}$ is then fitted to the I(Q) data and the result acts as the general phonon Q-dependence for that specific S(Q,E)-map (Fig. 3, upper left). Then, S(Q,E) is integrated over a region believed to have no magnetic intensity to generate the phonon partial density-of-states (pDOS) (Fig. 3, upper right). The general Q-dependence and pDOS are then extrapolated to a full S(Q,E)-map (Fig. 3, lower left) which is subtracted from the data to ideally yield the magnetic spectrum (Fig. 3, lower right). Unfortunately, this method did not replicate the phonon spectrum accurately in our case; the subtracted S(Q,E)-map has residual vibronic intensity, and no magnetic intensity, which would decrease with increasing Q, emerges.

Compound **(1)** and **(2)** are known to be particularly sensitive to air due to the reduced pyrazines, which spontaneously oxidise when exposed to air. To confirm that our powder

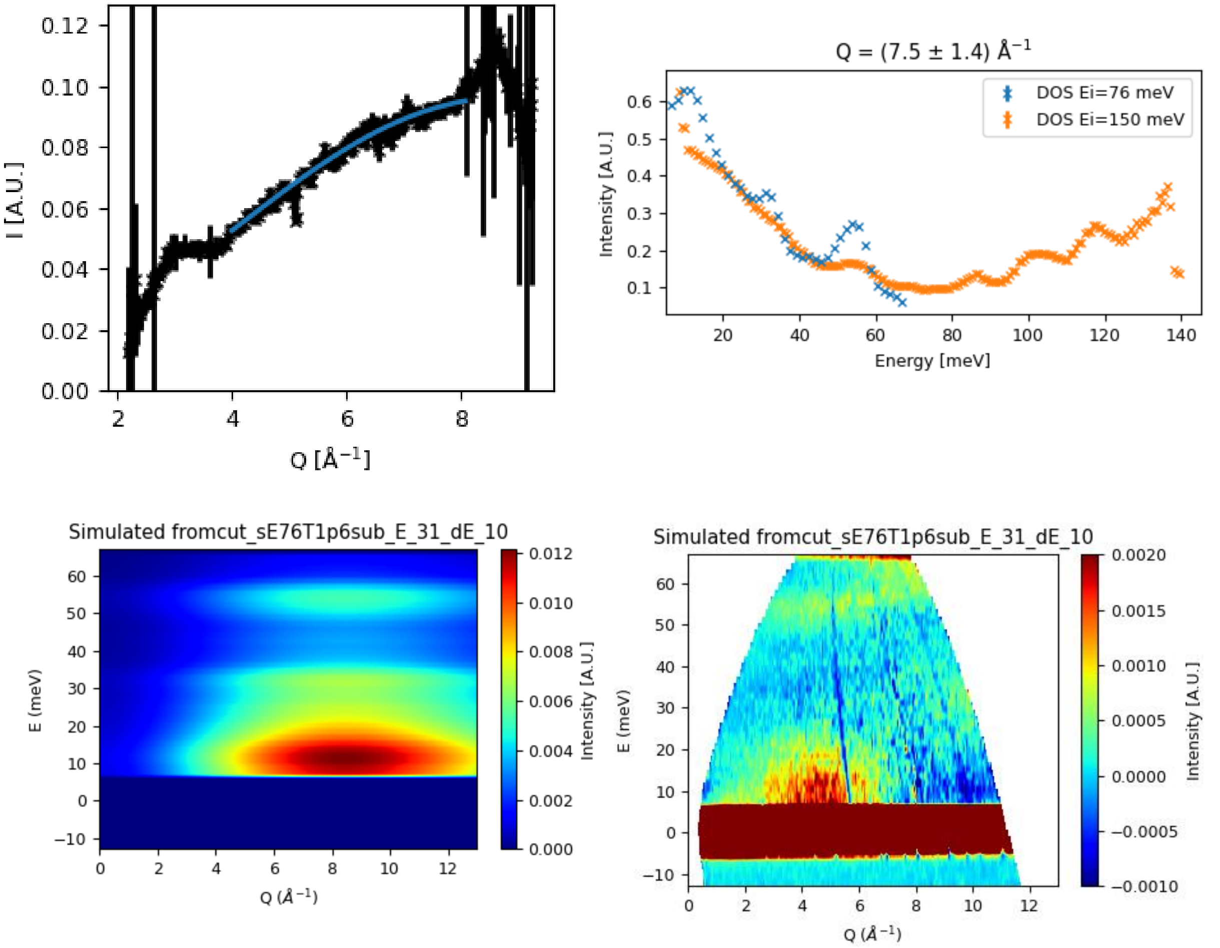

Fig. 3: Extrapolation of phonon spectrum of **(1)** from the non-magnetic part of measured S(Q,E) measured with E_i = 76 meV at T = 1.6 K (upper row, lower left) and final, phonon-subtracted spectrum (lower right).

sample of **(1)** had not degraded, we compared its measured pDOS to the vibrational spectrum of neutral and reduced pyrazine as studied in [1] using Raman spectroscopy and DFT. We found that the vibrational pDOS measured with neutrons accurately agreed with the Raman and DFT results on reduced pyrazine, which confirms that our sample of **(1)** had not degraded. A similar analysis for **(2)** was not possible, since deuteration is expected to change the vibrational spectrum of pyrazine (neutral and radical) and we have no reference for deuterated pyrazine.

Future Analysis

abINS2, which is currently under development at ILL, could be used to calculate the vibrational spectrum of pyrazine directly from the DFT results, which have been validated with Raman and now INS. If given the resolution function of PANTHER, abINS2 could give a more precise phonon spectrum for subtraction, which might reveal subtle magnetic features.

References

[1] P. Perlepe et al., Science 370, 587-592 (2020)
[2] S. Toth and B. Lake, J. Phys.: Condens. Matter 27, 166002 (2015)