Experimental report

03/08/2022

Proposal:	**EASY-929**	**Council:**	10/2020
Title:	Spin excitations in the valenced delocalized molecular magnet Fe-14		
Research area:	Chemistry		

This proposal is a new proposal

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Samples: [FeTp(CN)3]8[Fe(D2O)(DMSO)]6 where Tp- = hydrotris(pyrazolyl)borate, DMSO = dimethyl sulfoxide

Instrument	Requested days	Allocated days	From	To
IN5	24	24	30/08/2021	31/08/2021

Abstract:

Molecular magnets are finite clusters of metal ions distributed within a crystalline lattice such that their magnetic properties are molecular. Over the last decades such systems have represented ideal test beds to investigate the collective behaviour of unpaired electrons using inelastic neutron scattering. With ILL proposal 4-06-8, the first investigation of the spin dynamics within a molecular magnet exhibiting electron delocalisation due to mixed valency began. With this easy-proposal, we seek to finalize that investigation. The availability of a isotope-enriched sample will allow us to perform higher-resolution measurements with low incoming energy to investigate thermally populated transitions and complete the picture of the spin dynamics in a valence-delocalised molecular magnet.

Experimental Report – EASY-929

Introduction

The experiment performed as a result of proposal EASY-929 is a continuation of proposal 4-06-8, which set out to study double exchange spin dynamics in a valence-delocalised molecule for the first time in the molecule $[Fe^{2+}(Tp)(CN)_3]_8[Fe^{2.667+}(H_2O)(DMSO)]_6$ (abbreviated as Fe_{14}, Tp^- = hydrotris(pyrazolyl)borate, DMSO = dimethyl sulfoxide). Double exchange (DE) is an interaction mechanism between spins in mixed-valence compounds where the mixed valency causes delocalisation of the "extra" valence electron, which leads to spin polarization and hence ferromagnetic interactions. The goal of EASY-929 was to repeat selected measurements from 4-06-9 on a new, ^{11}B-enriched powder sample to minimise absorption, leading to better resolution and allow for use of neutrons with smaller E_i.

Fig. 1 shows some results from 4-06-9. Three molecular spin excitations were found at ca. 0.48, 0.64 meV and 0.95 meV labelled I, II and III, respectively. The intensity found in the areas inside the red circles are believed to be experimental artifacts. The excitations' magnetic origins were confirmed by their decrease in intensity with increasing Q.

Excitations I and II were not well separated, and it was unclear if a third excitation was hiding underneath. Furthermore, we could not separate well the hot excitations which appeared in the region 0.3-0.6 meV when measuring at T = 6 K. The goal of proposal EASY-929 was to solve these issues, and to perform a first measurement with λ_i = 10 Å which had not been possible previously due to absorption from the boron in the original Fe_{14} sample.

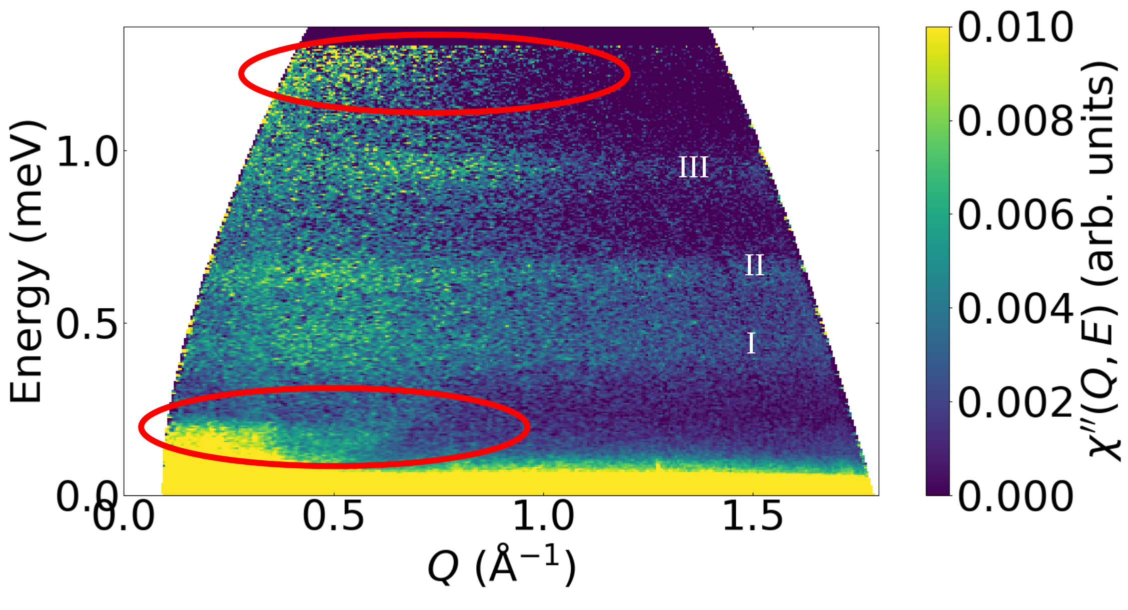

Fig. 1: S(Q,E) of Fe_{14} measured with IN5 using λ_i=6.5 Å at T = 1.6 K. Three distinct excitations are found and named I, II and III respectively. The intensities found inside the red areas are believed to be experimental artifacts

Results and initial analysis from EASY-929

Fig. 2-3 show the data obtained from EASY-292. Measurements with λ_i = 10 Å at T = 1.5 K revealed a new molecular spin excitation at 0.34 meV, which is now labelled I. Measurements with λ_i = 7.5 Å at T = 1.5 K refound the excitations at 0.48, 0.64 and 0.95 meV, which are now labelled II, III and IV, and confirmed the absence of other excitations in the 0.4-0.7 meV range. Due to the better resolution, peak II was also found on the anti-Stokes side of the elastic line, in line with the principle of detailed balance. The resolution with λ_i = 7.5 Å is not good enough to also see I on the anti-Stokes side. When keeping λ_i = 7.5 Å and heating to T = 6 K, all excitations from the ground state disappeared, and three hot bands appeared at 0.34 meV, 0.47 and 0.88 meV labelled i, ii, and iii, respectively.

To determine the exact excitation energies, we have fitted suitable peak shapes to data and included a background term when data reduction could not get rid of experimental artifacts. The λ_i = 10 Å was fitted with a gaussian line shape and a parabolic background, while Lorentzian line shapes and a constant background were used for the λ_i = 7.5 Å data. When fitting the T = 1.5 K data, the positions of II and II* are locked to be equidistant from E = 0. For the T = 6 K data, we were also able to account for the elastic peak in our fitting.

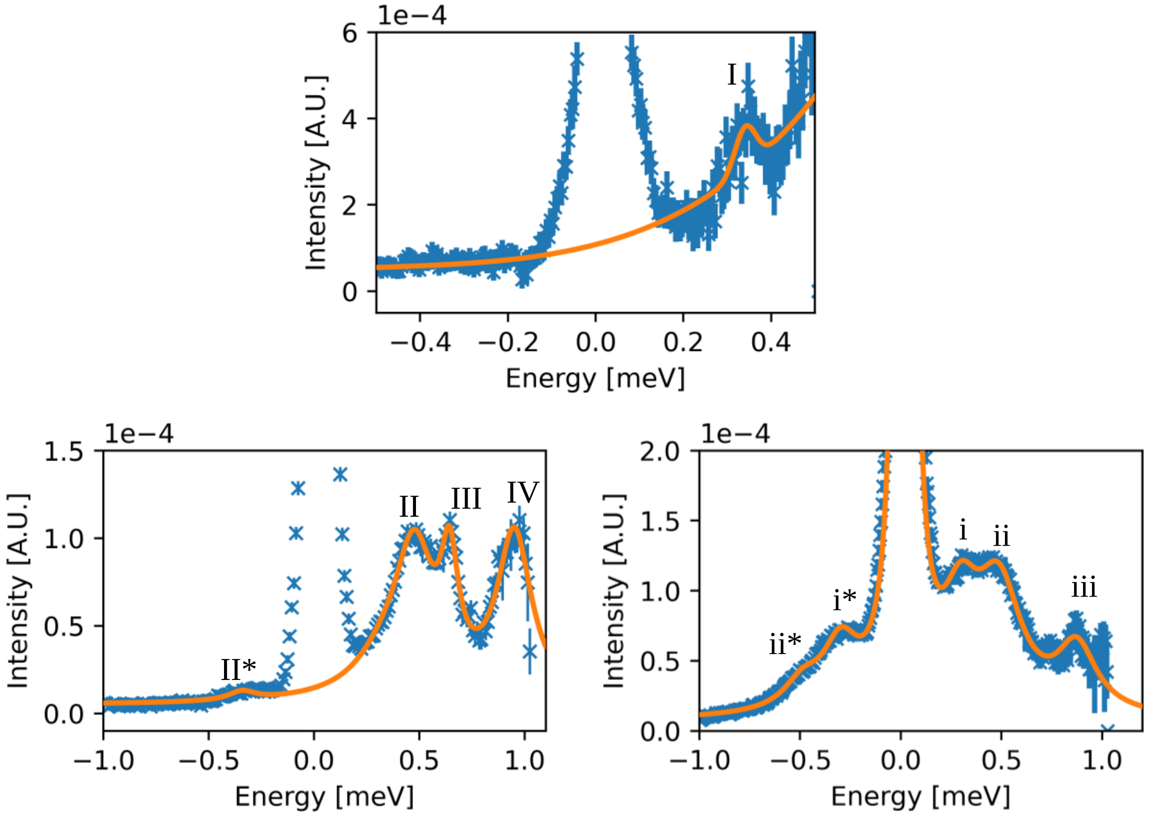

Fig. 2: S(E) of ^{11}B-enriched Fe$_{14}$ measured with IN5 using λ_i = 10 Å at T = 1.5 K (top) and using λ_i = 7.5 Å at T = 1.5 K (bottom left) and T = 6 K (bottom right). Excitations from the ground state are numerated with uppercase roman numerals in ascending order of excitation energy. Excitations from excited states are numerated with lowercase roman numerals in the same manner. Orange lines are fits to determine the excitation energies as described in the text. Asterisks mark the anti-stokes counterparts of the excitations on the Stokes side.

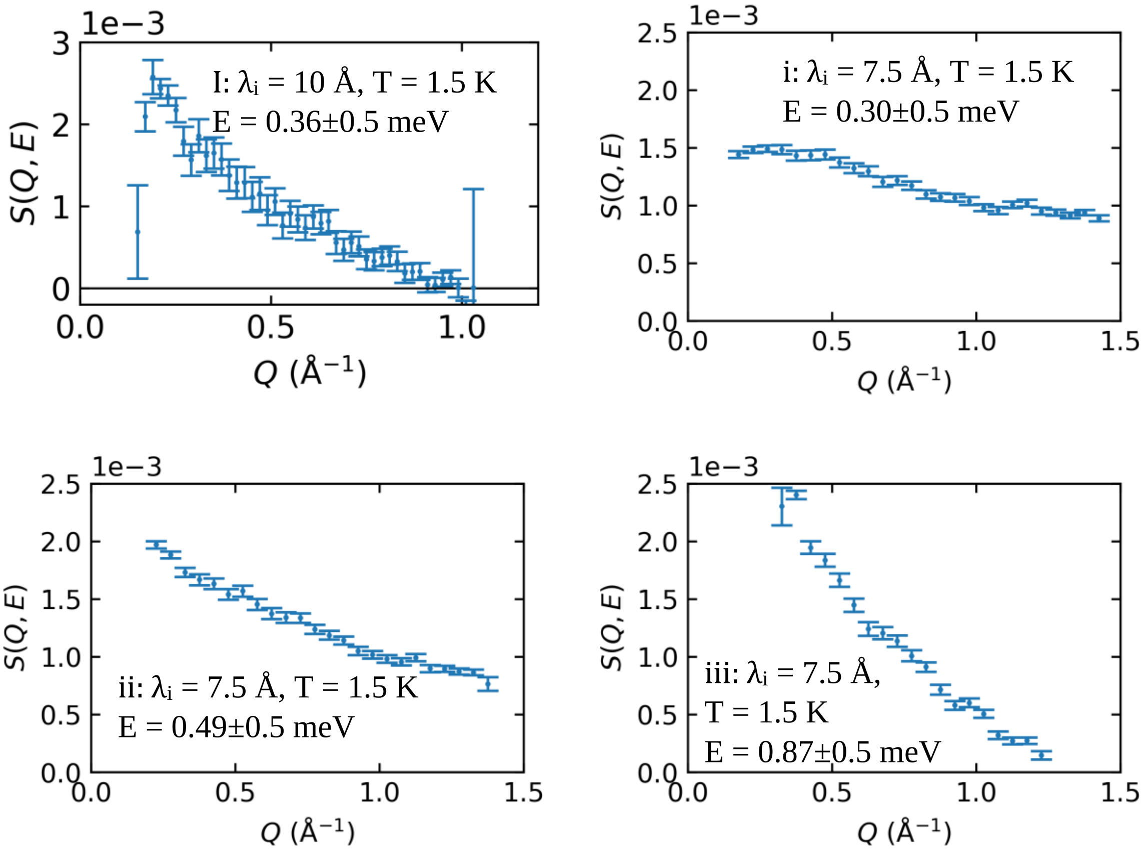

Fig. 3: S(Q) of ^{11}*B-enriched Fe*$_{14}$ *measured with IN5.*

The magnetic origin of all the discussed peaks were confirmed by examining their Q-dependences, which are shown in Fig. 3 and all decrease with increasing Q. While no distinct features can be observed in any of the S(Q) plots, they all have different slopes, which suggest that the underlying wavefunctions of the states involved in the transition differ between excitations.

Future Analysis

Analysis of the above data with a pure Heisenberg Hamiltonian model was not successful, hence double exchange needs to be accounted for as well. We are currently working on incorporating the FORTRAN program MVPACK [1] into our inhouse Matlab program which solves the neutron scattering equation for a given model containing both the Hamiltonian and structural information. This will allow us to gain insight into the role of double exchange in the spin dynamics of Fe$_{14}$.

References

[1] J. J. Borrás-Almenar et al, J. Comput. Chem., 31, 1321 (2010)