Experimental report

04/05/2022

Proposal: 5-31-2816 **Council:** 10/2020

Title: Tracking the magnetic phase transition of postperovskite metal thiocyanates

Research area: Physics

This proposal is a resubmission of 8-04-222

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Samples: CsM(NCS)3 M = Ni,Co,Mn

Instrument	Requested days	Allocated days	From	To
D1B	2	1	06/06/2021	07/06/2021
D20	2	0		

Abstract:

Dense coordination polymers combine the functional properties typical of the traditional inorganic solid state, such as magnetism, with the remarkable tunability and flexibility that arises for the incorporation of molecular components. They therefore offer the opportunity to discover unusual behaviour that arises from the coupling these properties. Thiocyanate compounds have the potential for rich optical and magnetic properties, but both their chemistry and magnetism remain comparatively unexplored.
In this proposal. we intend to study the family of CsM(NCS)3, M=Mn,Co,Ni, molecular analogues of the high pressure postperovskite structure. Our previous bulk magnetic measurements and experiments at the ILL show that all three of these compounds show significant spin canting and M=Co and Ni are weak ferrimagnets. This study by mapping out the temperature evolution of their complex magnetic structures, will complete our study of this family. It provide us with insight both into the design of new magnetic, molecular framework materials the magnetic behaviour of the important postperovskite structure type.

Tracking the magnetic phase transition of post-perovskite metal thiocyanates

This experiment was undertaken to measure three molecular post-perovskites, $CsM(NCS)_3$ M=Mn, Co, Ni. Data was collected to determine the ground state magnetic structure of these compounds and to follow the evolution of the magnetic ordering through their ordering temperatures.

Constant wavelength powder neutron diffraction data for $CsMn(NCS)_3$ and $CsNi(NCS)_3$ were collected on the high intensity medium resolution D1b diffractometer. The incident wavelength was λ = 2.52 Å and the scattering was measured over an angular range of $2 < 2\theta < 128°$. NOMAD software from the ILL was used for data collection.

It was not possible to carry out a measurement on for the cobalt analogue as a result of difficulties in scaling up the synthesis. No data were collected for this sample.

Thermal diffractograms for $CsMn(NCS)_3$ were collected between 1.5 K and 20 K heated with a programmed ramp of 0.06 K min^{-1}. Long acquisition measurements were collected at 1.5 K and 20 K.

The data from the thermal ramp have been processed and plotted as a 3-dimensional heatmap. The most intense magnetic peaks have been plotted as a function of temperature, so the decrease in intensity can be tracked as the ordering temperature (16 K) is reached and surpassed.

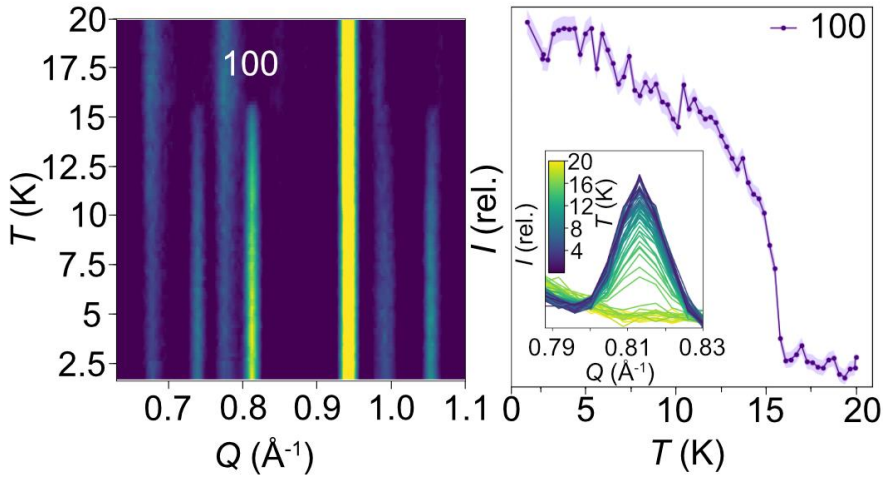

Figure 1. Left: thermal diffractogram of $CsMn(NCS)_3$ measured between 1.5 and 20 K. Right: The intensity of the 100 magnetic Bragg reflection at 0.81 $Å^{-1}$ is followed as a function of temperature.

Thermal diffractograms for $CsNi(NCS)_3$ were collected between 1.5 K and 10 K heated with a programmed ramp of 0.025 K min^{-1}. Long acquisition measurements were collected at 1.5 K and 10 K.

A refinement of the ground state magnetic model was completed using the FullProf program using the data collected from the long acquisition at 1.5 K. It was determined that, like it's nuclear structural space group, $CsNi(NCS)_3$ has the magnetic space group $P2_1/c$. It has two types of

magnetic nickel atoms, one where the moments align antiferomagnetically, and the other where the moments order as a weak ferromagnets. These moments are canted with an angle of 46.5°, which results in a net magnetic moment of 0.78 μ_B along the *b* axis.

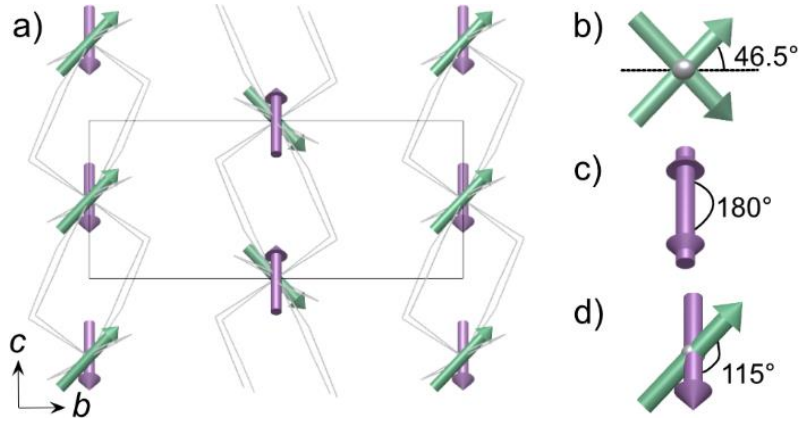

Figure 2. Magnetic structure of $CsNi(NCS)_3$, the two unique magnetic vectors are represented with purple arrows for the antiferromagnetic component and green arrows for the weak ferromagnetic component; a) Magnetic unit cell viewed along a *axis; b) canting angle between the weak ferromagnetic moments; c) ordering of the antiferromagnetic moments; d) the ordered magnetic moments projected onto a single atom.*

The data obtained from the ramp has been plotted as a heat map and the prominent magnetic peak, indexed to be the 100 reflection, can be followed as a function of temperature.

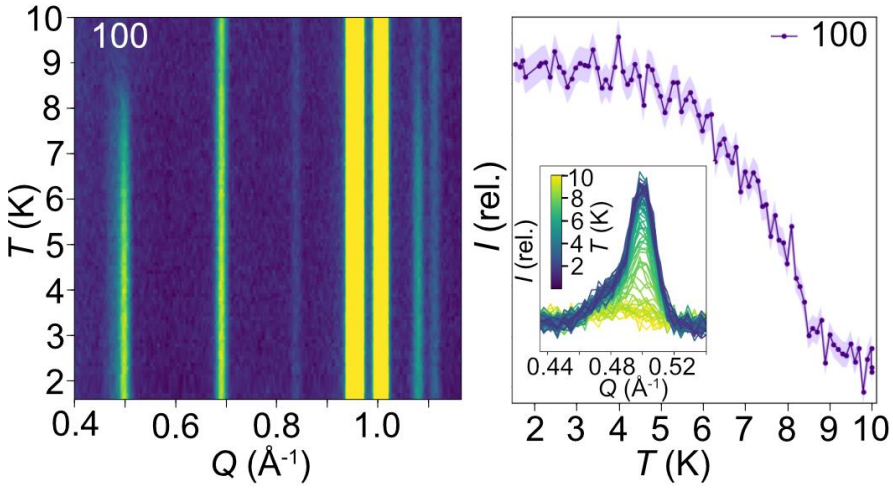

Figure 3. Left: Diffraction pattern of $CsNi(NCS)_3$ measured between 1.5 and 10 K. Right: The intensity of the 100 magnetic peak at 0.49 $Å^{-1}$ is followed as a function of temperature.

These data have been used in combination with other experiments carried out at ILL (5-12-344, 5-41-1060, 5-31-2767) as part of the thesis for a current ILL PhD student and the results are currently being written up to be published in a widely read journal.