Experimental report

29/04/2022

Proposal: **5-24-660** **Council:** 10/2020

Title: Evolution of magnetic ordering under pressure in low-dimensional pseudohalides

Research area: Materials

This proposal is a new proposal

Main proposer: **Matthew CLIFFE**

Experimental team: Madeleine GEERS
Oscar Ramon FABELO ROSA
Ines PUENTE ORENCH

Local contacts: Laura CANADILLAS DELGADO
Oscar Ramon FABELO ROSA
Ines PUENTE ORENCH
Vivian NASSIF
Claire COLIN

Samples: $Ni(NCS)_2$

Instrument	Requested days	Allocated days	From	To
D2B	0	2	02/06/2021	04/06/2021
D20	2	0		
D1B	2	2	31/05/2021	02/06/2021

Abstract:

Molecular framework materials have attracted much recent attention due to their extreme responses to stimuli and the ability to design structure. In contrast to conventional (oxide, halide) frameworks, by choosing metals and linkers, we can effectively target specific structures and therefore functionality. One challenge in harnessing this tunability to design e.g. future device materials, is that molecular linkers do not facilitate strong magnetic interactions. Here we propose the systematic investigation of the thiocyanate-based molecular framework, namely nickel (II) thiocyanate, $Ni(NCS)_2$. Unlike other molecular frameworks, thiocyanate has been shown to be able to facilitate strong magnetic coupling ($|T_{CW}| > 100$ K; $Ni(NCS)_2$ $T_N = 54$ K) while retaining flexibility not found in the analogous halide frameworks. We have found a dramatic increase in T_N for this framework under hydrostatic pressure. To understand this magnetoelastic coupling, we will measure the magnetic ground state at low temperature and high pressure, and the evolution of the magnetic and nuclear structure on heating at high pressure.

Evolution of magnetic ordering under pressure in low-dimensional pseudohalides

This experiment was undertaken to look at the effect of applied pressure on the structural and magnetic properties of the binary pseudohalide $Ni(NCS)_2$. The binary transition metal thiocyanates, $M(NCS)_2$, are two-dimensional materials which have analogous structures to the halide compounds MX_2. Applying external pressure to the halide compounds can result in elevated magnetic ordering temperatures, and bulk magnetic measurements show a similar trend for $Ni(NCS)_2$. Neutron diffraction measurements were carried out to determine the structural and magnetic basis for the observed trend in ordering temperatures.

The bulk magnetic susceptibility measurements have been recorded between ambient pressure and 5.8 kbar, which shows an increase in the Néel temperature (T_N) from approximately 54 to 63 K. Measurements were carried out at 3, 4.5 and 6.7 kbar on the high intensity, medium resolution D1b powder diffractometer to collect data on the magnetic changes to the material. Following this, measurements at 1.7, 3.4, 5.1 and 6.7 kbar were carried out on the high resolution D2b powder diffractometer, to follow the structural variations with pressure.

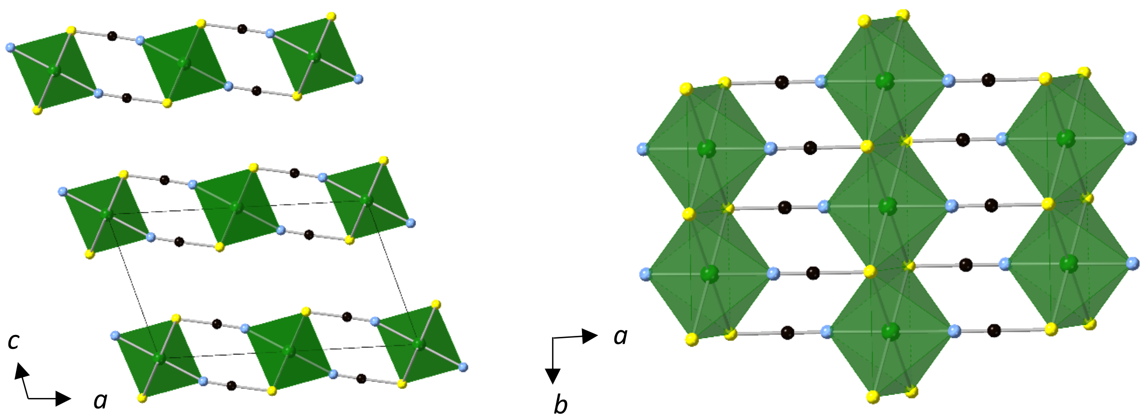

Fig. 1. Nuclear structure of $Ni(NCS)_2$ viewed along the b axis showing the stacking of the layers (left) and one layer viewed along the c axis (right).

The measurements on the D1b diffractometer were carried out with an incident wavelength of 2.52 Å and the scattering was measured over an angular range of $2 < 2\theta < 128°$. Thermal diffractograms of $Ni(NCS)_2$ were collected over the range of the T_N: 3 kbar: 30 – 65 K; 4.5 kbar: 40 – 65 K; 6.7 kbar: 30 – 70 K, with a programmed ramp of 0.05 K min^{-1} (0.07 K min^{-1} for measurement at 4.5 kbar). External pressure was applied with a He gas cell.

It was not possible to obtain reliable measurements for sample at 6.7 kbar as there was a leak in the gas cell at 43 K. Two further attempts at 6.7 kbar was made, however it was not possible to cool below 50 K, so not further measurements were made at this pressure. This leak was able to be fixed before the measurements on the D2b diffractometer were carried out.

The measurements on the D2b diffractometer were collected with an incident wavelength 1.60 Å and the scattering was measured over an angular range of $10 < 2\theta < 160°$. Long acquisition measurements were made at room temperature with applied pressures of 1.7, 3.4, 5.1 and 6.7 kbar. Data were also collected at the temperature points 20, 40 and 180 K for 6.7 kbar.

Rietveld refinements will be made using FullProf for the data collected on the D2b diffractometer to track any changes in the lattice parameters at each pressure point collected. The data obtained from the D1b experiment will be plotted as heatmaps to observe the evolution of the magnetic peaks as a function of temperature at each applied pressure.

The results from this experiment will form part of the thesis for a current ILL PhD student and will be published in a widely read journal.

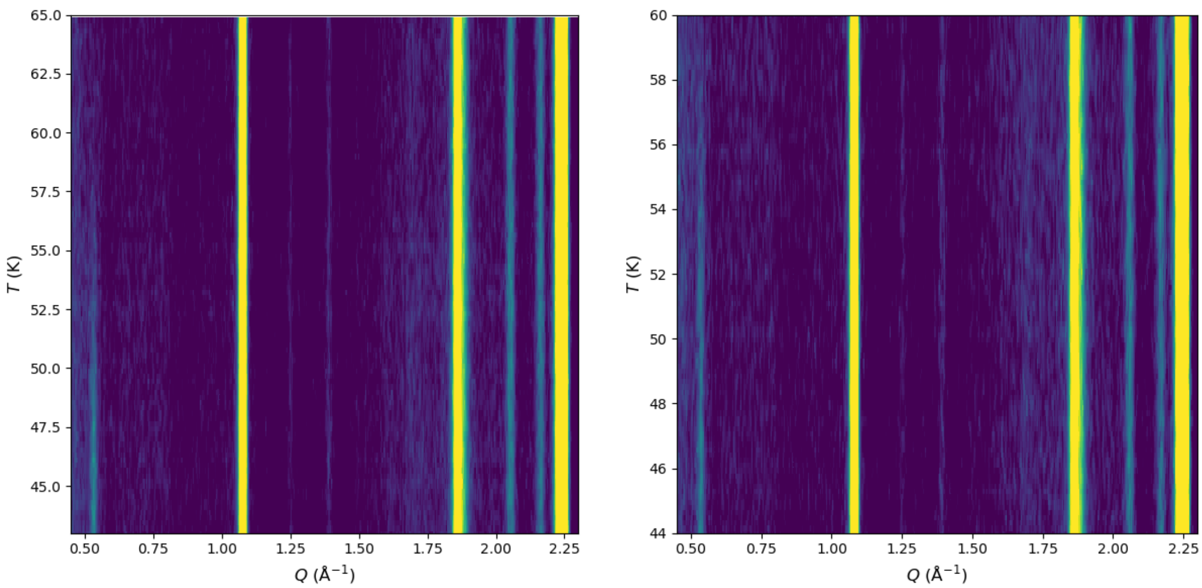

Fig 2. Diffraction patterns of $Ni(NCS)_2$ under 3 kbar (left) and 4.5 kbar (right). The most prominent magnetic Bragg reflection is observed at 0.52 $Å^{-1}$ and 0.53 $Å^{-1}$.