Experimental Report

03/03/2014

Proposal: **5-31-2284** **Council:** 10/2012

Title: Magnetic order in urea-based Mn2-Nb(CN)8 chiral molecular magnetand in its non-chiral counterpart

This proposal is a new proposal

Researh Area: Physics

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Samples: (1) [Mn(urea)2(H2O)]2[Nb(CN)8]
(2) [Mn(H2O)2]2[Nb(CN)8].4H2O

Instrument	Req. Days	All. Days	From	To
D20	2	1	27/02/2013	28/02/2013

Abstract:

The proposal considers two 3D molecular magnets: optically active chiral [Mn(urea)2(H2O)]2[Nb(CN)8], Tc = 43 K (sample A) and the non-chiral [Mn(H2O)2]2[Nb(CN)8].4H2O of Tc = 47 K (sample B). The compounds belong to the TII-L-[Nb(CN)8] family, (T = Mn, Fe Ni, L = nonmagnetic organic ligand) which shows various type of functionalities. The structure is tetragonal, space group for A is P41 and for B - I4/m. A and B are soft ferrimagnets with magnetization of saturation at T= 2 K equal to 9 Bohr magnetons permol. Our plan is to determine the order of magnetic moments below the transition temperature for both compounds. We apply for 2 days at the D20 diffractometer, lambda=2.4 Å, T=300 K, 2 K, 20 K, 30 K, 40 K, 50 K and 150 K. Due to the crystallographic complexity, data should be taken with the Soller collimator to assure good resolution. For the neutron diffraction experiment samples A and B will be prepared in the deuterated form and checked with XRD, magnetic and IR measurements.

Final report

Ex Number: **5-31-2284** Instrument **D20** 27/02/2013 - 28/02/2013

Magnetic order in urea-based Mn_2-$Nb(CN)_8$ chiral molecular magnet and in its non-chiral counterpart

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Introduction

Neutron diffraction experiment has been performed on deuterated samples of two molecular magnets:

- sample **A** - $[Mn(urea)_2(H_2O)]_2[Nb(CN)_8]$, (in short ureaMn2Nb)
- sample **B** - $[Mn(H_2O)_2]_2[Nb(CN)_8]\cdot 4H_2O$, (in short Mn2Nb).

The compounds exhibit 3D frameworks based on cyanido-bridges linking Mn^{II} and Nb^{IV} centers. The urea ligand $CO(NH_2)_2$ molecule, leads to formation of an optically active chiral network (sample **A**), which shows second harmonic generation (SHG), strongly enhanced below magnetic transition temperature T_c of 43 K. Sample **A** can be relatively easily transformed to the sample **B,** which is a non-chiral magnet of T_c = 47 K and may be regarded as a reference sample. According to D. Pinkowicz et al. (Chem. Mater. **23** 2011 21) and J.M. Herrera et al. (C.R. Chimie **11** 2008 1192) the compounds belong to the tetragonal system, space group $P4_1$ (**A**) and I4/m (**B**). Unit cell dimensions are equal to a=10.450(5) Å, c=22.736(4) Å for sample **A** and a=12.080(2) Å, c=13.375(4) Å for **B**.

Experimental

Powder samples of ca. 1 g (**A**) and ca. 0.5 g (**B**) were packed to the vanadium container (ϕ=8 mm) and placed in the orange cryostat. Neutrons wave length was 2.41 Å, the D20 instrument worked in the high resolution mode. The following diffraction patterns in the 2θ range 0.1^o-150^o were obtained:

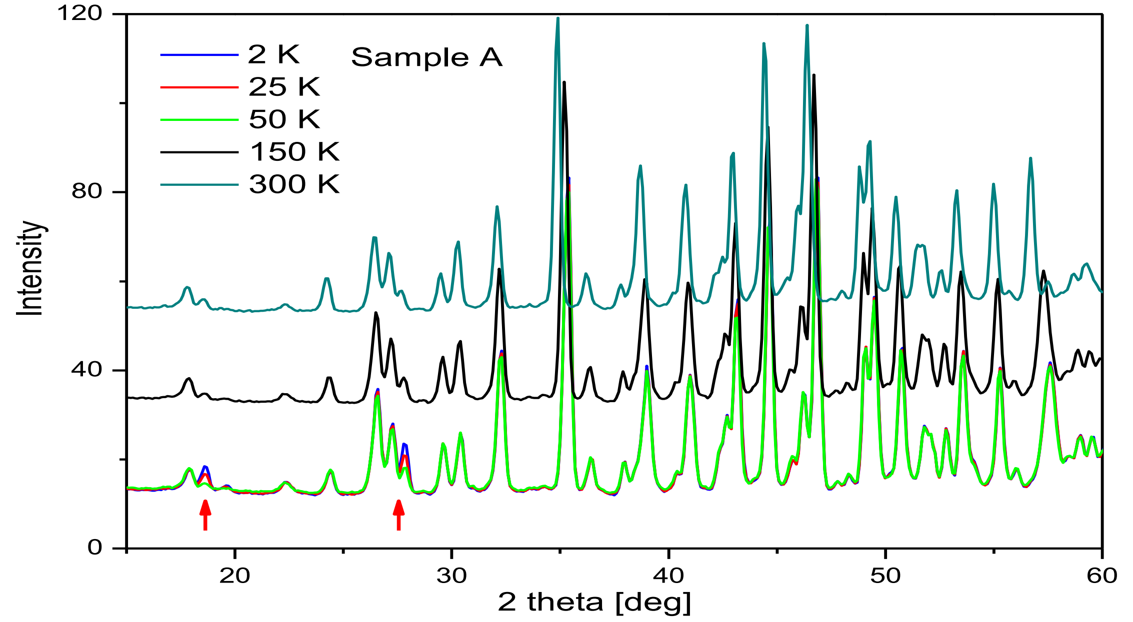
Sample **A** (ureaMn2Nb): long runs at constant temperature 300 K, 150 K, 50 K, 40 K, 25 K and 2 K and a series of short runs during the temperature change;

Sample **B** (Mn2Nb): runs at constant temperature110 K, 50 K and 2 K and a series of short runs during the temperature change.

When cooled below the appropriate T_c, both samples showed magnetic contribution to the intensity of some neutron reflections. No extra reflections were observed.

Results - Sample A

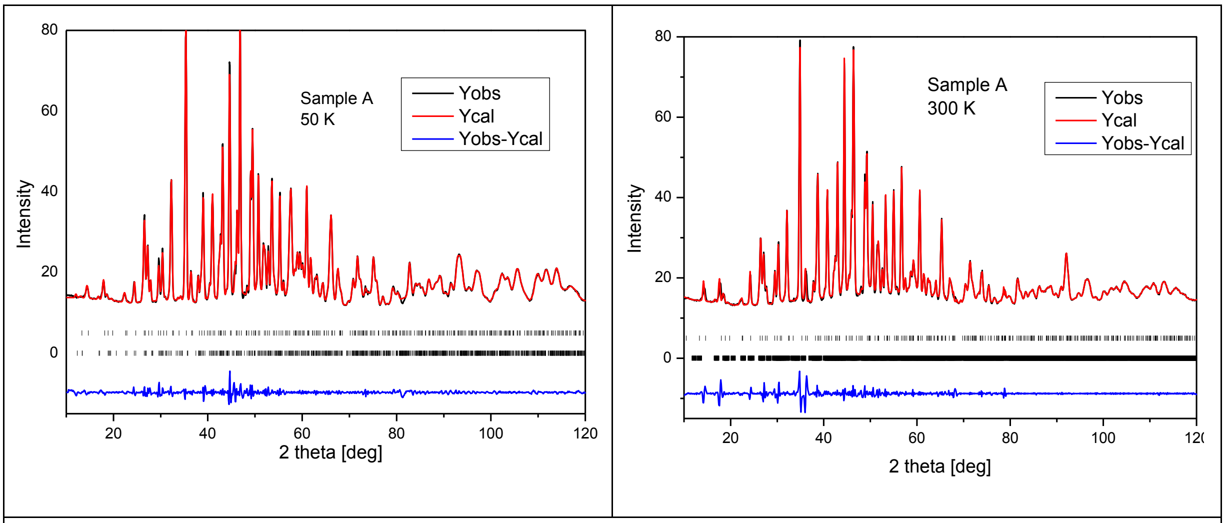
In order to refine the crystal structure of **A** above T_c, the data recorded at 50 K, 150 K and 300 K have been worked-out using the Fullprof programme. It appeared, that in addition to the main chiral **Aα** phase (Space group P 4_1) the patterns contained contribution from the centric **Aβ** polymorph (Space group P -1). This parasitic β phase was not discovered with the XRD check before the ND experiment because of the very similar structure and peaks overlap.



Neutron diffraction patterns in the $2\theta = 15^o$-60^o range for sample **A** of T_c=43 K at different temperatures (shown). Red arrows point to the reflections with strongest magnetic contribution observed at 2θ = 18.65 deg and 119.62 deg.

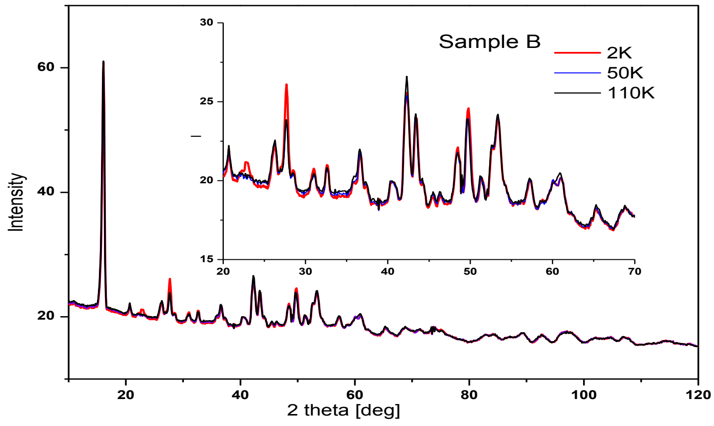
The table below gives the unit cell parapeters determined for the **Aα** phase (Space group P 4_1) and for the **Aβ** polymorph (Space group P -1).

	a	b	c	alpha	beta	gamma
Aα 50 K	10.416167	10.416167	22.484581	90.000000	90.000000	90.000000
Aβ 50 K	10.446829	10.438538	11.445728	82.993385	82.219284	88.371002
Aα 300 K	10.408245	10.408245	22.914141	90.000000	90.000000	90.000000
Aβ 300 K	10.451903	10.448380	11.490791	83.051971	82.435600	88.189262



The fitted (LeBail method) diffraction patterns for sample **A** at T = 50 K and 300 K showing the presence of the additional **β** phase of the structure similar to that of the **α** phase.

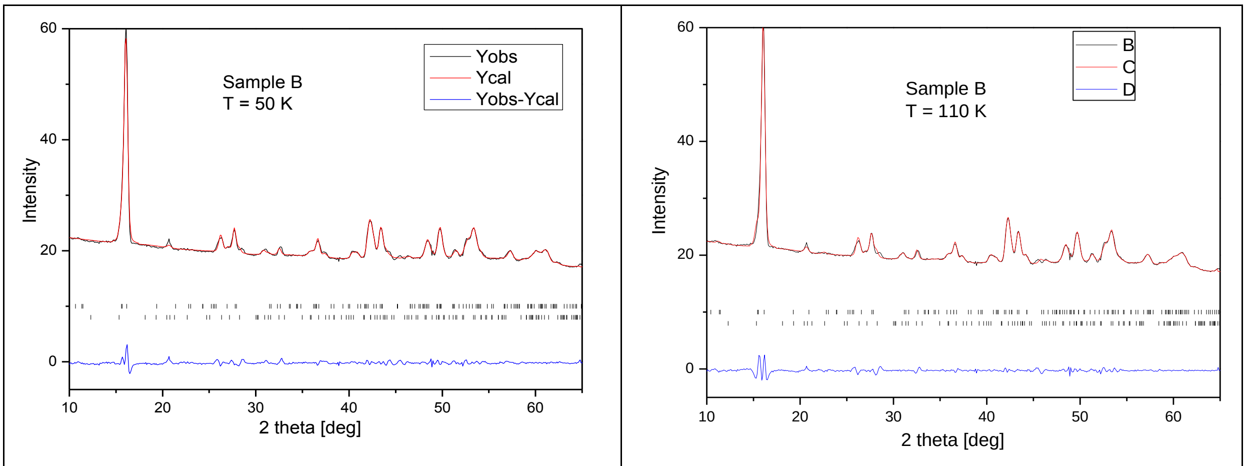
Results - Sample B



Neutron diffraction patterns for sample **B** of T_c=47 K at different temperatures (shown). Reflections with strongest magnetic contribution appear at 2θ = 22.25, 22.85, 27.02 27.67 and 41.77 deg .

The reference sample **B** appeared to be also contamined with the secondary phase and consited of the expected **B1** phase (Space group Pmmm) and of unwanted **B2** phase (Space group P 21/n). The table below gives the unit cell parapeters determined for the **B1** and **B2** phase at T = 50 K and 110 K.

	a	b	c	alpha	beta	gamma
B1 50 K	12.982722	12.075404	12.194000	90.000000	90.000000	90.000000
B1 50 K	7.326292	14.378647	18.065590	90.000000	90.000000	90.000000
B2 110 K	13.253606	12.073117	12.194001	90.000000	90.000000	90.000000
B2 110 K	7.331159	14.374569	18.078699	90.000000	90.000000	90.000000



The fitted (LeBail method) diffraction patterns for sample **B** at T = 50 K and 110 K showing the presence of the expected **B1** phase (Space group Pmmm) and the unwanted **B2** phase (Space group P 21/n).

Conclusion

Because of the presence of the unwanted extra phases of the similar structure determined in **A** and **B** samples, it was not possible to separate the individual contributions and to analyse the spectra below the T_c ordering temperatures. After successful synthesis of the deuterated, single phase sample **B**, we would like to continue this subject and submit a next proposal.