Experimental report

17/07/2016

Proposal: 5-31-2382 **Council:** 10/2014

Title: Determination of magnetic structure in Mn2-Nb(CN)8 molecular magnet

Research area: Physics

This proposal is a continuation of 5-31-2284

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Samples: [MnII(H2O)2]2[NbIV(CN)8].4H2O

Instrument	Requested days	Allocated days	From	To
D20	1	1	21/07/2015	22/07/2015

Abstract:

The aim of the project is determination of magnetic structure in molecular material [Mn(H2O)2]2[Nb(CN)8].4H2O (1), the outbound system of the family of compounds showing interesting functionalities. 1 is a soft ferrimagnet with Mn (S=5/2) and Nb (s=1/2) sublattices and Tc of 47 K. Experiment no. 5-31-2284, performed at D20 for the partially deuterized sample, revealed, aside from 1 (s.g.: I 4/m), the presence of the parasitic phase 2 (s.g.: P 21/c). The phase 2 has not been discovered with XRD performed before the ND experiment, because of peaks overlap of 1 and 2. The reason for appearance of the secondary phase 2 was most probably heavy water used for the synthesis of the deuterized sample. We would like to repeat the experiment for the new, non-deuterized powder sample, synthesized according to the verified procedure using H2O. As shown in experiment 5-31-2284, in spite of large incoherent background, the crystallinity of the material ensures good quality of ND data. We would like to obtain patterns at T = 300 K and 2 K (2*4 hours) and at 10 K, 20 K, 30 K, 40 K, 50 K, 150 K (ca. 12 hours). We apply for 1 day at D20, lambda = 2.4 Å.

Final report

Ex Number: **5-31-2382** Instrument **D20** 20/07/2015 - 21/07/2015

Determination of magnetic structure in Mn_2-$Nb(CN)_8$ molecular magnet

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Introduction

Neutron diffraction experiment has been carried out for the $[Mn(H_2O)_2]_2[Nb(CN)_8]\cdot 4H_2O$, (in short Mn2Nb) molecular magnet with T_c = 47 K. The former neutron diffraction study conducted on the partially deuterized sample (experiment no. 5-31-2284) revealed, aside the expected crystallographic phase (s.g.: *I*4/*m*), also the intensity coming from the secondary parasitic phase (s.g.: *P* 21/*m*). The present measurements were performed on the new sample which was synthesized according to the verified procedure using H_2O. The compound belongs to the materials showing potential functionalities [1] and is a soft ferrimagnet with magnetization of saturation at $T = 2$ K equal to 8.6 μ_B/mol, as expected for the antiferromagnetic coupling of Mn and Nb sublattices (S_{Mn}=5/2, S_{Nb}=1/2, $g_{Mn,Nb}$=2) [2].

Experimental and results

Diffraction patterns at wave length 2.4 Å were obtained in the 2θ range 0.1°-150° for T = 2 K, 20 K, 40 K, 62 K, 100 K and 300 K. When cooled below T_c, the sample showed one extra peak and some magnetic contribution to the intensity of several neutron reflections (Fig. 1).

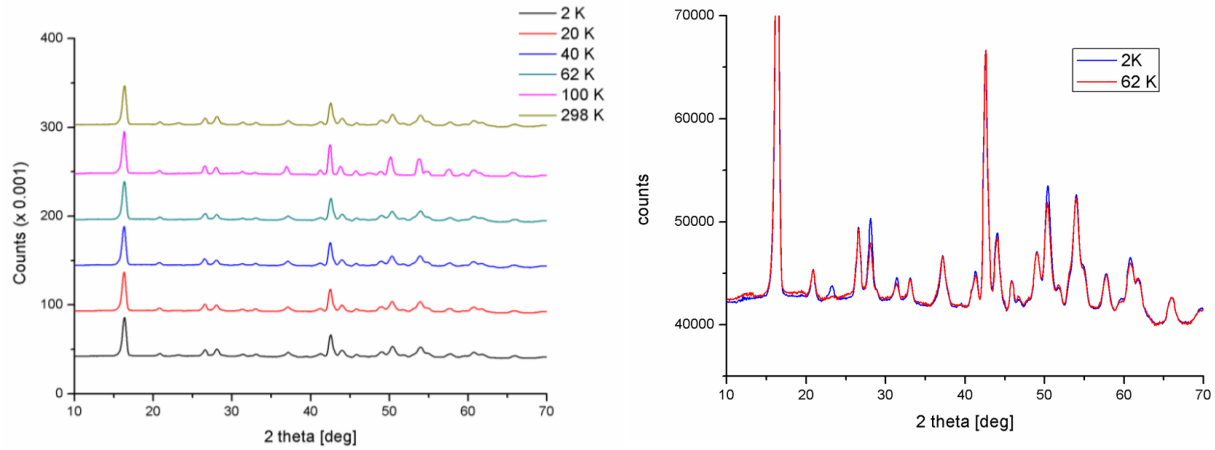
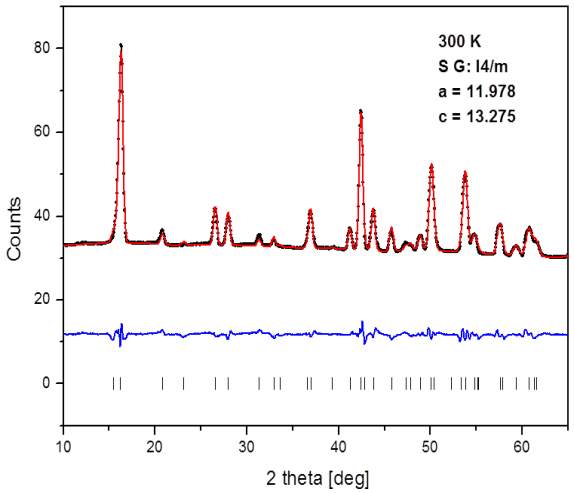


Fig. 1 All neutron diffraction patterns obtained for the $[Mn(H_2O)_2]_2[Nb(CN)_8]\cdot 4H_2O$ sample of T_c = 47 K (*left*) and patterns below and above T_c (T=2 K and T=62 K) (*right*).

As followed from the single crystal X-ray diffraction at 300 K [3], Mn_2Nb belongs to the tetragonal system, space group *I*4/*m*, with unit cell dimensions a = 12.080(2) Å, c = 13.375(4) Å. ND pattern at T = 300 K could be indeed described by the *I*4/*m* space group, a = 11.978 Å, c = 13.275 Å. Fig. 2 presents the Rietveld fit in the real space of the structure without hydrogen atoms, together with the positions of Nb, Mn, C, O, and N atoms. However using the space group *I*4/*m* for working-out the patterns at T = 100 K and T = 62 K delivered

the worse result and the data could be better described with the orthorhombic *I 112/m* space group or even the *Pmmm* group. Fig. 3 shows the pattern at T = 62 K together with the fit using *I 4/m* (left) and *I 112/m* space groups (right).



Atom	x	y	z
Nb1	0.00000	0.00000	0.193(2)
Mn1	0.349(5)	-0.923(6)	0.00000
C1	0.130(2)	0.1177(20)	0.1613(11)
C2	0.4881(20)	0.2654(17)	-0.1438(14)
N1	0.2653(11)	0.0823(11)	0.1250(10)
N2	0.4059(17)	0.3916(18)	-0.1538(6)
O1	0.428(3)	0.106(3)	0.00000
O2	0.332(3)	0.6131(16)	0.00000
O3	0.185(2)	0.2332(19)	0.115(2)

Fig. 2 Neutron diffraction pattern at T = 300 K and Rietveld fit using the *I*4/*m* space group, in the real space without hydrogen atoms. Right: positions of Nb, Mn, C, O, and N atoms.

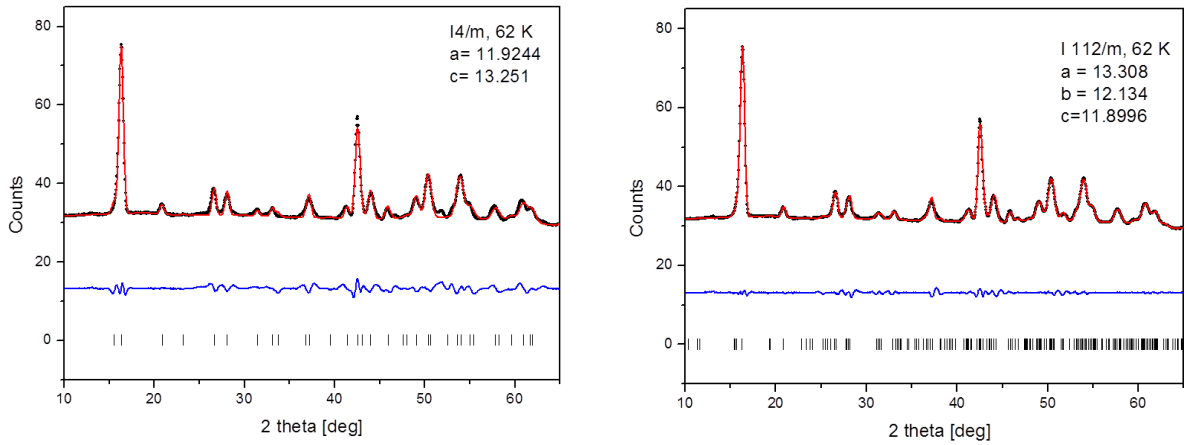


Fig. 3 Neutron diffraction pattern at T = 62 K and the Rietveld fit in real space using the *I*4/*m* (left) and *I 112/m* (right) space groups.

In the situation of the uncertainty in the crystal structure and the possibility of the phase transition on lowering of the temperature, the synthesis of the single crystal of the compound and the X-ray diffraction study have been carried out. The tendency to crystal twinning and migration of water molecules in the structure was observed. It was concluded that the next step should be to perform the simultaneous synchrotron and neutron investigations on the sample of the large mass obtained in one synthesis.

[1] B. Sieklucka, R. Podgajny, D. Pinkowicz, B. Nowicka, T. Korzeniak, M. Bałanda, T. Wasiutyński, R. Pełka, M. Makarewicz, et al. CrystEngComm, **11** (2009) 2032.

[2] D. Pinkowicz, R. Podgajny, W. Nitek, M. Rams, A.M. Majcher, T. Nuida, Shin-ichi Ohkoshi, B. Sieklucka, Chem. Mater. **23** (2011) 21.

[3] J.M. Herrera et al. C.R. Chimie **11** (2008) 1192.