Experimental report

06/02/2016

Proposal:	**5-15-607**	**Council:**	4/2015

Title: Pressure-dependence of the structure of the molecular multiferroic material (ND4)2[FeCl5(D2O)]

Research area: Materials

This proposal is a new proposal

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Samples: (ND4)2[FeCl5(D2O)]

Instrument	Requested days	Allocated days	From	To
D10	0	0		
D9	18	12	30/11/2015	12/12/2015

Abstract:

The compound (ND4)2[FeCl5(D2O)] has awakened a renewed interest owing to its recent classification as a new multiferroic material. We have recently investigated by means of single crystal neutron diffraction the magnetic structure at zero magnetic field of (ND4)2[FeCl5(D2O)], observing a cycloidal magnetic structure propagating in the c-axis with k = (0, 0, 0.23) and with the magnetic moments lying in the ac plane. Furthermore, we have investigated the influence of pressure in the magnetic structure using CYCLOPS Laue diffractometer. From this previous experiment we have observed a dependence of the magnetic structure with the hydrostatic pressure. The variation of the magnetic structure is closely related with slight variations in the crystal structure, thus monochromatic neutron diffraction is necessary to determine accurately the crystal structure under pressure. Therefore in this proposal we intend to study the effect of moderate pressures in the crystal structure of this compound by means of single crystal neutron diffraction.

Pressure-dependence of the magnetic structure of the molecular multiferroic material $(NH_4)_2[FeCl_5(H_2O)]$

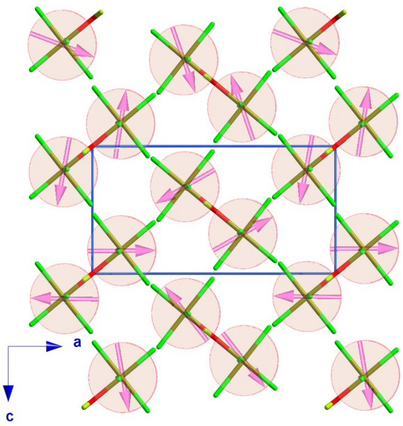

Figure 1: View along the *b*-axis of the superposition of the magnetic structure of $(ND_4)_2[FeCl_5(D_2O)]$. The counterions have been omitted for the sake of clarity.

The $(NH_4)_2[FeCl_5(H_2O)]$, has awakened a renewed interest owing to its recent classification as a new multiferroic material.[1] This compound orders antiferromagnetically at $T_N = 7.25$ K and multiferroicity arises below *ca.* 6.9 K. We had recently investigated, by means of single crystal neutron diffraction at D9 diffractometer, the magnetic structure of $(ND_4)_2[FeCl_5(D_2O)]$ in order to understand the underlying mechanism of multiferroicity in this compound.[2] This example represents the first molecular material that presents coupling between the magnetic and electric orders, and therefore is the first example of improper ferroelectricity for molecular systems. We have observed at zero magnetic field a cycloidal magnetic structure propagating in the *c*-axis with $\mathbf{k} = (0, 0, 0.23)$ and with the magnetic moments lying in the *ac* plane (Figure 1).[2] This cycloid would be at the origin of the magneto-electric coupling via inverse Dzyaloshinsky–Moriya interaction.[3]

The main objective of the present experiment was the evaluation of the influence of pressure in the cationic network. In order to understand magneto-structural correlations of this compound under external pressure, the accurate determination of the nuclear structure is extremely important. With this objective we applied for 18 days of beam time in order to collect 5 point of pressure. However, in the allocated beam-time (12 days) was only possible to make full data collections at two pressure points in the paramagnetic phase, at 5 kbar and at 7.5 kbar (nominal pressure). Some experimental problems together with the difficulty of the crystal orientation within the pressure cell impeded us to collect a last pressure point at around 10 kbar, as requested in the proposal.

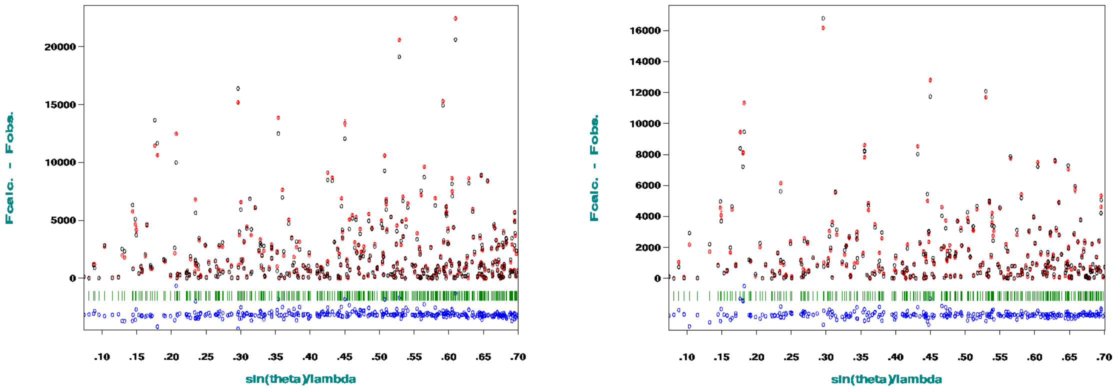

Figure 2: Plots of the F_{cal}-F_{obs} *vs* $\sin(\theta)/\lambda$ collected at 40K at the D9 instrument under an external pressure of 5 (left) and 7.5 kbar (right). The experimental data are represented as red circles (o) the calculated are represented as black circles (o) and the difference as blue circles (o). The vertical green marks correspond with the Bragg reflections compatible with the $P112_1/a$ space group.

The data analysis of both pressure points collected in the paramagnetic phase show that a full structural refinement is possible. The crystal structure determinations at 5 kbar and 7.5 kbar were done using 712 and 583 independent reflections, respectively. However, some issues related with the absorption correction due to the pressure cell are still to be solved. A plot with F_{cal}-F_{obs} *vs* $\sin(\theta)/\lambda$ for both refinement is shown in Figure 2. This initial data treatment shows not only slight variations in the crystal structure, but also a change in the extinction parameters, which is related with micro-domain effects.

We also undertook a survey of the pressure-induced changes in the magnetic propagation vector. At 5 kbar the propagation vector was shifted less than expected based in previous measurements. From the scan of different magnetic reflections a propagation vector of **k** = (0, 0, 0.22) was determined. At 7.5 kbar, after the evaluation of different Q-scans, we determined a propagation vector **k** = (0, 0, 0.19). Therefore we have proved that the variation in the external pressure is enough to modulate the propagation vector. However, this modulation is rather different of those obtained applying external magnetic field. In that case, the increase of the magnetic field produces an increase of the modulation period, varying from **k** = (0, 0, 0.23) to **k** = (0, 0, 0.25) for external magnetic field ranged from 0 to 4.5 T.[4]

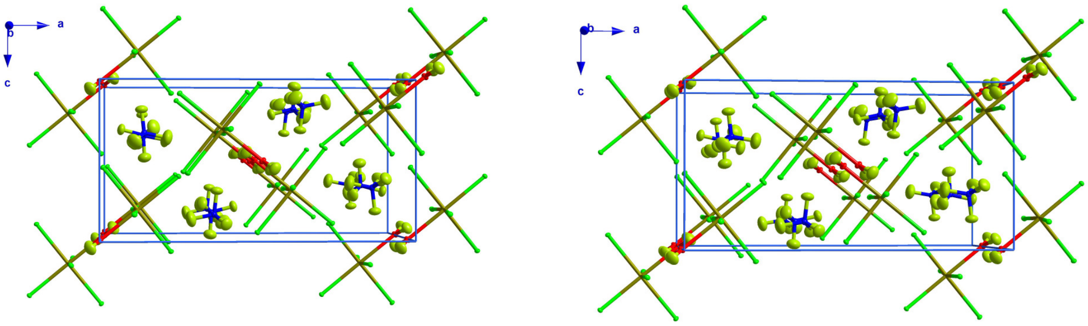

Figure 3: View of the crystal packing of the $(ND_4)_2[FeCl_5(D_2O)]$ compound obtained from the D9 data refinement at 40K and 5 (left) and 7.5 kbar (right). The green, gold, red and lime atoms represent the chlorine, iron, oxygen and deuterium atoms respectively. The atoms refinement has been done using anisotropic thermal parameters and the figures represent the atoms in ellipsoid mode.

As in previously reported compounds (see A. J. Schultz *et al.*[5]), pressure induces slight variations in the Cl···Cl and in the O-D···Cl distances (see figure 3), being the shortest distances those obtained for the 7.5 kbar pressure point. The evolution of these distances as a function of the external pressure can be correlated with the modification of super-exchange coupling. This feature can explain the variation observed in the propagation vectors and therefore in the magnetic structures.

To obtain final conclusions about the influence of the pressure on $(ND_4)_2[FeCl_5(D_2O)]$ compound, we are going to apply for extra beam-time in D9 diffractometer in order to carry out at least an extra pressure point at 11 kbar (nominal pressure) to evaluate the expected full transformation from incommensurate magnetic structure to commensurate, and to obtain a full structural model at this pressure in the paramagnetic phase.

References

[1] Ackermann M, Brüning D, Lorenz T, Becker P and Bohatý L **2013** New J. Phys. *15* 123001

[2] Proposal 5-41-770. Experiment done at D9 single crystal diffractometer at zero-field and ambient pressure. Results published in: Rodríguez-Velamazán, J.A.; Fabelo, O.; Millán, A.; Campo, J.; Johnson, R.; Chapon. L. **2015,** Scientific Reports *5*:14475

[3] Mostovoy M **2006** Phys. Rev. Lett. *96* 067601

[4] Manuscript u*nder preparation*

[5] Schultz, A J, Carlin R L, **1995** Acta Cryst., *B51*, 43-4