Experimental report

27/08/2022

Proposal: **5-31-2820**

Council: 10/2020

Title: Refinement of the magnetic and nuclear structures in the hybrid multiferroic layered Perovskite-Like $(C_6H_5C_2H_4NH_3)_2FeCl_4$ compound

Research area: Materials

This proposal is a new proposal

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Samples: $(C_6H_5C_2H_4NH_3)_2FeCl_4$

Instrument	Requested days	Allocated days	From	To
D2B	1	1	29/06/2021	30/06/2021
D20	2	1	15/09/2021	16/09/2021

Abstract:

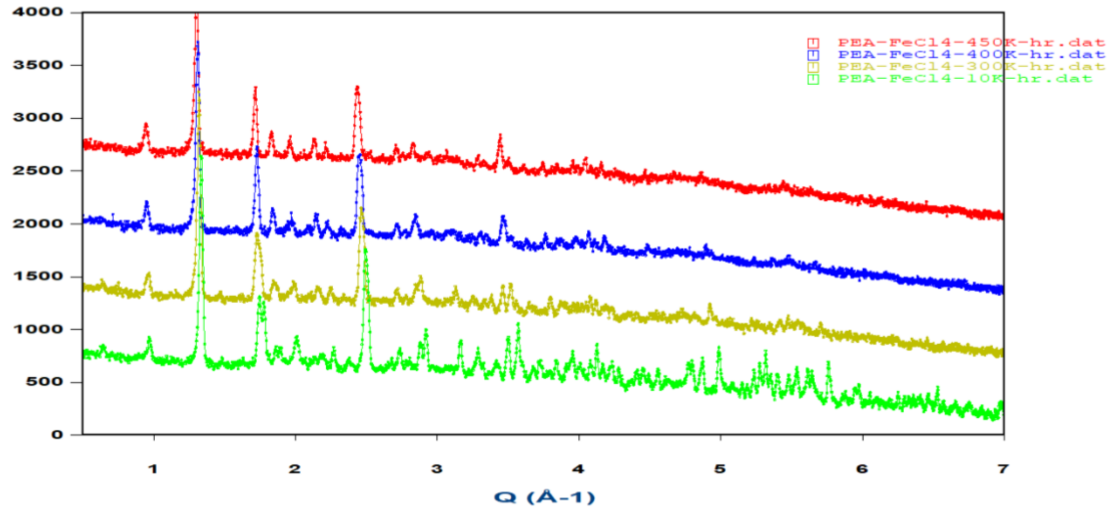
$(C_6H_5C_2H_4NH_3)_2Fe^{II}Cl_4$ is the first example of an organic-inorganic perovskite to exhibit coupling of ferro-elasticity and ferromagnetism below TC=98K and ferro-elasticity at TC=433 K. This is shown by switching the magnetic hysteresis on and off by uniaxial pressure through the strong coupling of the magnetic and elastic domains. In this proposal we intend to refine all the different nuclear and magnetic structures reported for the title compound in order to understand the evolution of the H bridges network that produce all the series of phases transitions and how the system reaches its long range magnetic order. For that reason we apply for 1 day at D20 high flux diffractometer to perform a thermal diffractogram from 1.8 to 480 K and 1 day at D2B to collect 4 high resolution difractograms at 1.8, 300, 400 and 480K.

Report of experiment 5-31-2820:

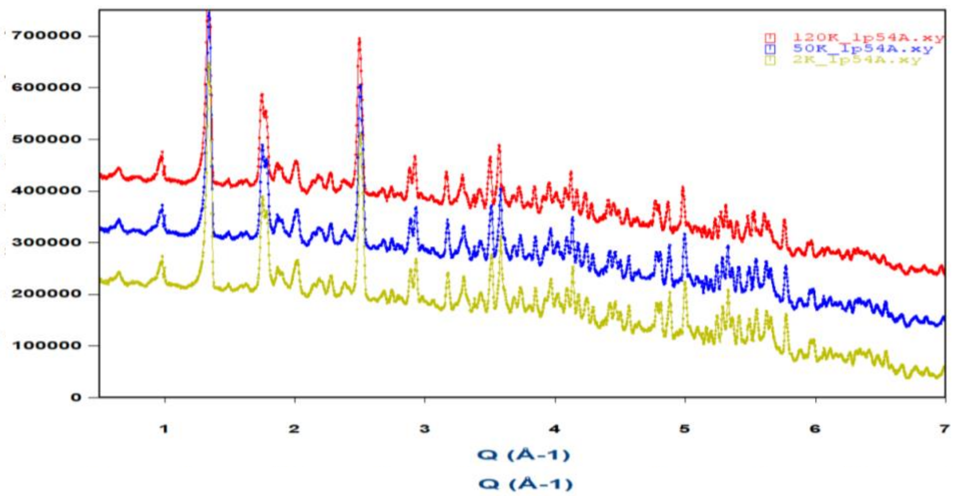
Title: Refinement of the magnetic and nuclear structures in the hybrid multiferroic layered Perovskite-Like $(C_6H_5C_2H_4NH_3)_2FeCl_4$ compound

This experiment was performed in ILL (Grenoble, France) at D2B from 29/06/21 to 30/06/21 (24 hours) and at D20 from 15/09/21 to 16/09/21 (24 hours). Several measurements were performed on a sample of $(C_6H_5C_2H_4NH_3)_2FeCl_4$ powder inside an 8mm vanadium holder:

- Measurements at D2B with λ = 1.594 Å for different temperatures: 10, 300, 400 and 460 K.

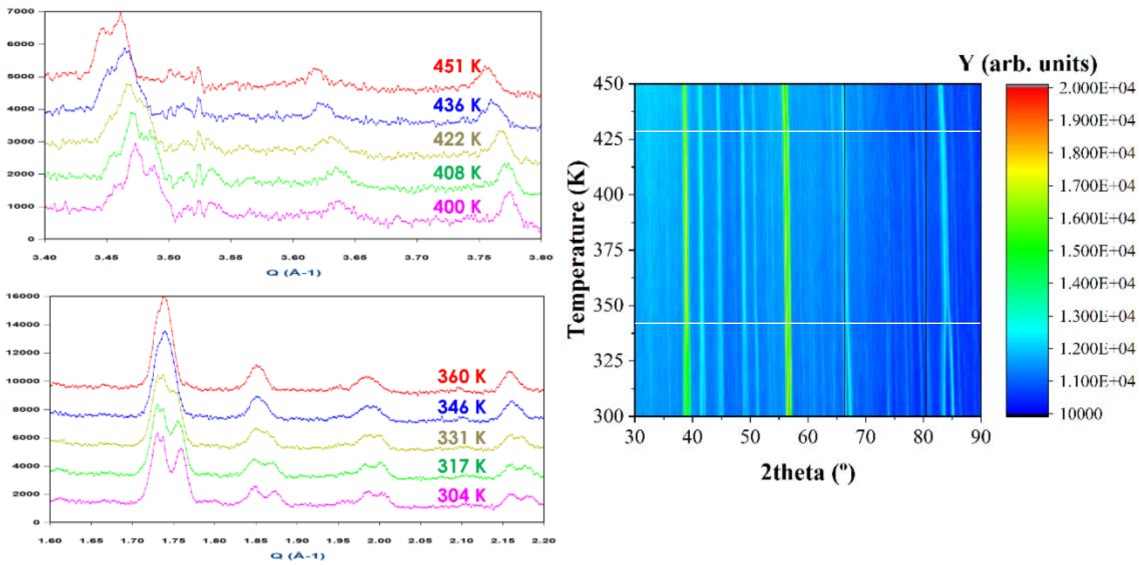


- Measurements at D20. First, data were taken with λ = 1.54 Å as the system was cooled down from RT to 2 K, performing measurements at fixed temperatures 120, 50 and 2 K. Then, measurements as the system was heated back from 2 to 460 K were taken with λ = 2.41 Å. Data points were taken at fixed temperatures 2, 50, 120, 300, 400 and 460 K, plus temperature ramps between each of these temperatures (thermodiffractograms).



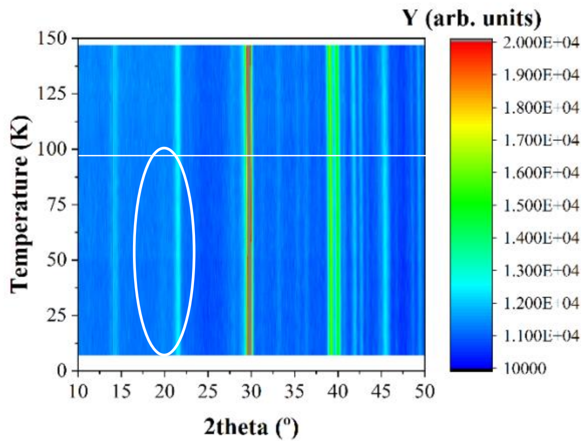
Phase transitions:

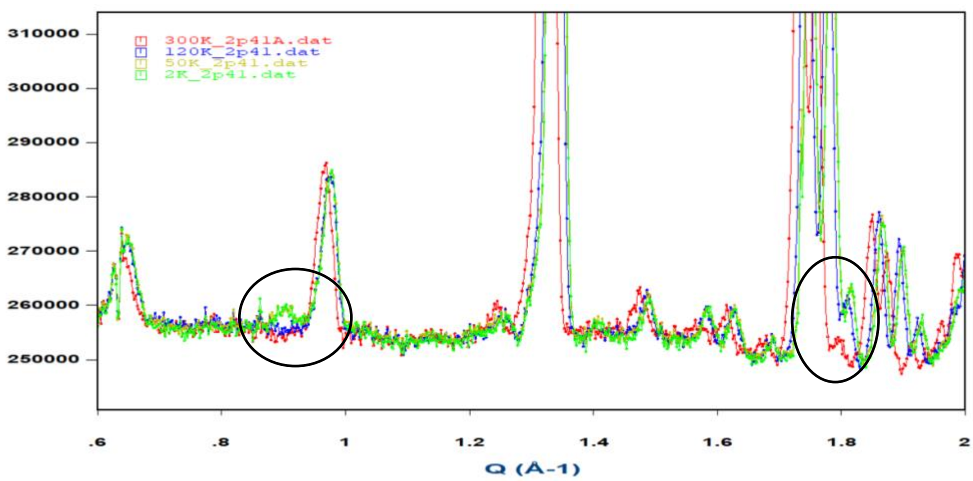
From the thermodiffractograms taken at D20 with λ = 2.41 Å, we can observe two phase transitions. The first one is observed around 340(10) K, where some peaks are merged as the temperature is increased. Similarly, a second phase transition is observed around 430(10) K.



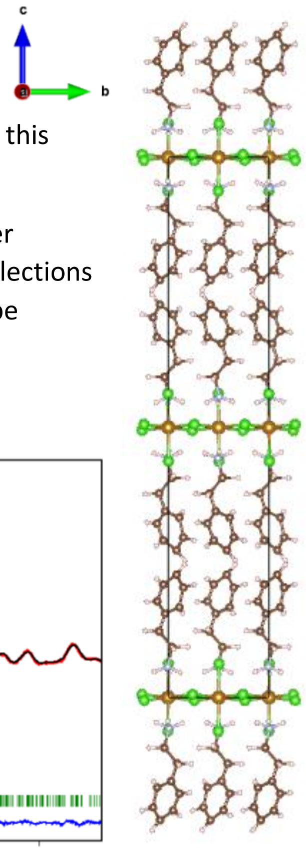
These structural phase transitions observed are in agreement with the DSC measurements associated with the change from Pbca to Bbcm at 343 K and the Bbcm to I4/mmm change at 433 K.

Regarding the low temperature regime, no structural phase transition is observed in the thermodiffractograms measured from 2 to 300 K. If we compare the data taken at fixed temperatures, an additional peak is observed at 2 and 50 K around Q = 0.9 Å, while a peak around Q = 1.8 Å increases its intensity. This suggests the onset of a long-range magnetic order, which is estimated to appear around 97(7) K from the thermodiffractograms data.



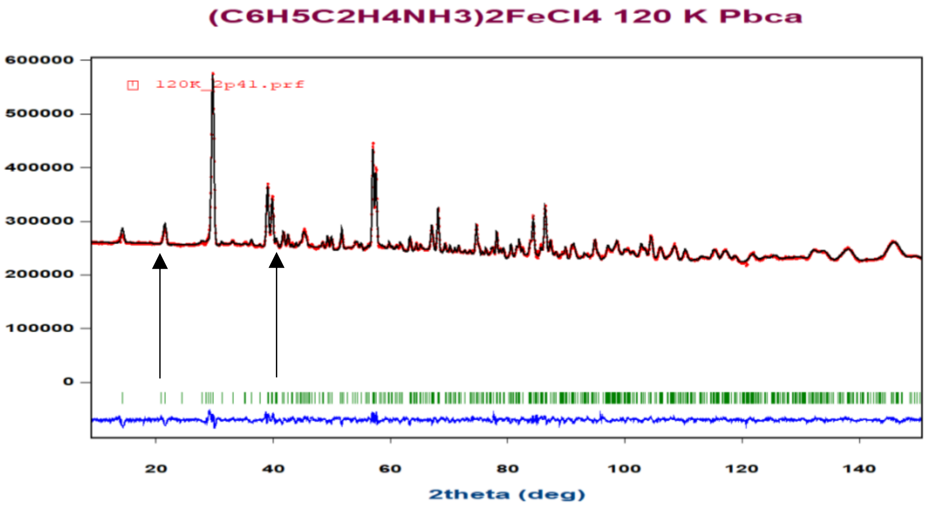


Refinement:



The analysis is focused on the low temperature part, where the magnetic transition occurs. As it is shown, the 300 and 120 K data can be well described by the model with space group Pbca (No. 61). A table with all the refinement parameters is given at the end of this report.

It is possible to observe that the two magnetic signals we see at lower temperatures (black arrows) are in the same positions as allowed reflections of Pbca space group, which implies that the magnetic structure can be described by a propagation vector $\vec{k} = (0, 0, 0)$



To describe the symmetry of this magnetic phase we use the irreducible representation theory, which tells us that the magnetic representation for the Fe atom in position 4b for the space group Pbca and propagation vector $\vec{k} = (0, 0, 0)$ is:

$$\Gamma = 3\Gamma_1(1) + 3\Gamma_3(1) + 3\Gamma_5(1) + 3\Gamma_7(1)$$

From the magnetization data we know that the magnetic structure has to be a canted antiferromagnet along the a-axis (CAF-a). If we compare this CAF-a with the magnetic structures from the irreducible representations, only the $\Gamma_7(1)$ allows such structure.

The fit to the 2 K data is very similar for all the representations, as it can be seen in the table below. However, the key difference is the fit to the magnetic peak around $2\theta = 20^{\circ}$, which is best described by the $\Gamma_7(1)$ magnetic structure.

IR	R_{Bragg}	$R_{Magnetic}$	χ^2	$\vec{m} \parallel a - axis$	$\vec{m} \parallel b - axis$
$\Gamma_1(1)$	8.39	53.1	36.4	1.3(4)	2.0(3)
$\Gamma_3(1)$	8.47	73.7	36.6	0.8(8)	1.2(4)
$\Gamma_5(1)$	8.24	55.1	36.1	2.8(2)	0
$\Gamma_7(1)$	8.34	58.2	36.2	0	2.6(2)