Experimental report

16/09/2019

Proposal:	**EASY-298**	**Council:**	4/2017
Title:	Magnetic structure of NaLaPrFeO6		
Research area:	Materials		

This proposal is a new proposal

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Experimental team:	
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Samples:	NaPrFeWO6

Instrument	**Requested days**	**Allocated days**	**From**	**To**
D1B	6	6	26/10/2018	27/10/2018

Abstract:

We here propose the determination of the magnetic ground state of NaPrFeWO6 sample. This compound belongs to the family of doubly ordered perovskites. It is characterized by a layered ordering of Na+ and Pr3+ cations perpendicular to the [0,0,1] direction of the primitive cell and a rock-salt ordering of Fe2+ and W6+ cations that can be seen as alternating layers of both cations perpendicular to the body diagonal of the parent cubic cell. The coexistence of both orderings favors the adoption of a polar crystal structure (space group P21; No 4) which makes it very valuable in the world of multiferroic oxides. The coexistence of both orderings is rare and only a limited number of examples are known so far. According to our knowledge, this is the first time that NaPrFeWO6 has been prepared for study. Magnetic measurements have shown an anomaly at TN=23 K and M(H) curves revealed spontaneous magnetization at 5 K. The aim of this easy access is to collect neutron patterns below and above TN to determine the magnetic ground state of this sample.

Magnetic structure of NaLaPrFeO_6

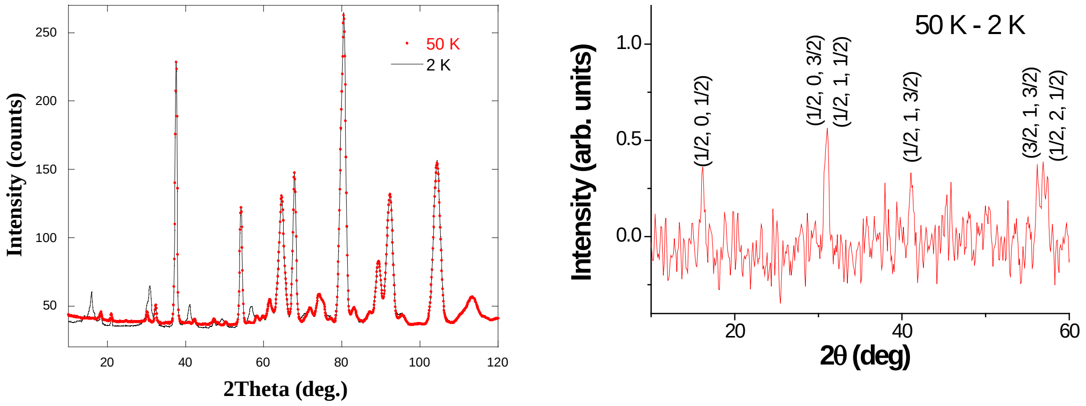

Figure 1. Left: neutron powder patterns at 50 (points) and at 2 K (line) for NaPrFeWO_6. Right: Pattern obtained by the difference between the previous neutron patterns. Indexation of the new weak magnetic peaks is also shown.

NaPrFeWO_6 was prepared by a sol-gel method using a modified citrate route [1]. The sample was characterized by powder x-ray diffraction (XRD) using Cu K$\alpha_{1,2}$ wavelengths. XRD pattern for NaPrFeWO_6 agrees with a doubly ordered AA'BB'O_6 perovskite with tilting distortions of B(B')O_6 octahedra according to the $a^-a^-c^+$ tilt system in the Glazer's notation [2]. The specimen also shows minor impurity phases: NaPrWO_4 and Na_2WO_4.2(H_2O). It was refined in the monoclinic space group $P2_1$, also reported for related compounds [3]. Magnetic measurements disclose the presence of a magnetic transition at low temperature with a clear peak at T_N~23 K in the M(T) curve [1]. In order to ascertain the magnetic ordering of this compound, neutron thermodiffractograms were measured between 2 and 50 K at the high intensity powder diffractometer D1B (λ=2.52 Å). A reference measurement at room temperature (RT) was also recorded. No significant differences were observed between the neutron patterns obtained at RT and at 50 K. However, clear changes are noticeable when the neutron diagrams measured at 50 and 2 K are compared (see Fig. 1). New magnetic peaks indexed as (h/2, k, l/2) are visible at 2 K (see Fig. 1).

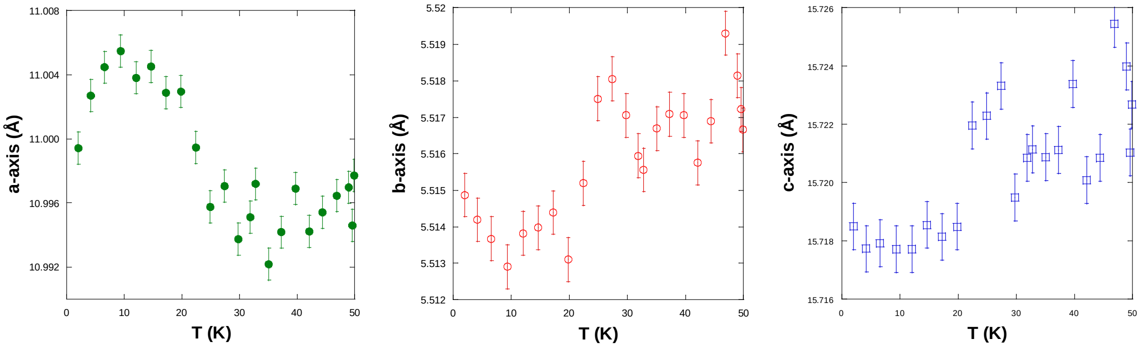

Figure 2. Evolution with the temperature of the refined lattice parameters for NaPrFeWO_6.

The new magnetic peaks appear below ~23 K and the magnetic transition is accompanied by a small change in the unit cell. Specifically, there is a small expansion of the a-axis while the other two lattice parameters follow the expected thermal contraction with decreasing temperature as can be seen in the Fig. 2. The occurrence of the abovementioned magnetic peaks specifies that the magnetic arrangement follows the propagation vector $\mathbf{k}$=(1/2, 0, 1/2) (A-point of the Brillouin Zone) as reported for related compounds [3]. We have used Isodistort program [4] to explore the magnetic irreducible representations for the nuclear cell with $P2_1$ symmetry. The search was limited to the A-point in agreement with the previous propagation vector. The corresponding magnetic space group (MSG) is polar (like its parent supergroup): P_a2_1 (4.10) and the lattice parameters of the magnetic unit cell in the standard setting are derived from the nuclear ones using the lattice vectors: $\boldsymbol{a}_M$= (2, 0, 0), $\boldsymbol{b}_M$= (0, 1, 0) and $\boldsymbol{c}_M$=(-1, 0, 1). Fig. 3 shows the Rietveld refinement and the magnetic structure following this standard setting. The refined lattice parameters a 2 K for $NaPrFeWO_6$ are a_M= 11.0046(8) Å, b_M= 5.4971(4) Å, c_M= 9.5567(6) Å and β=124.822(4)°. This unit cell corresponds to the smallest primitive magnetic cell.

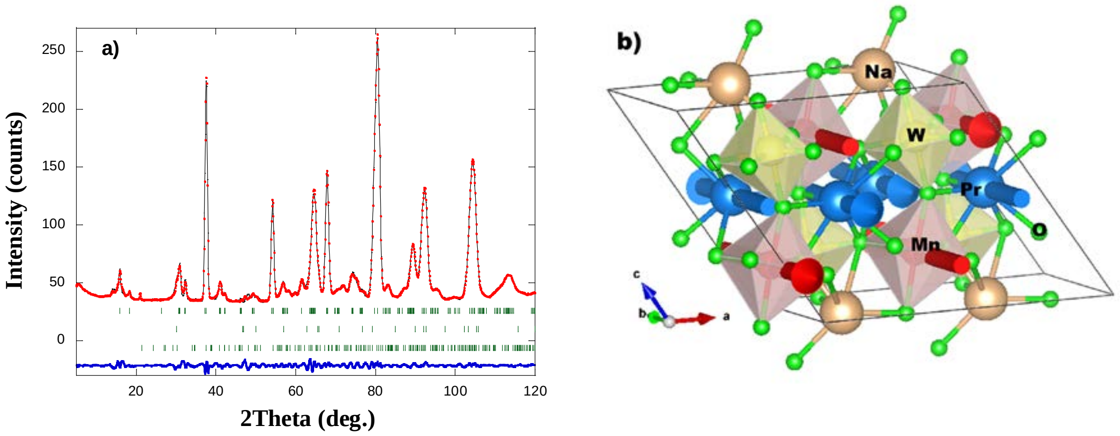

Figure 3. a) Rietveld analysis of the neutron diffraction pattern for $NaPrFeWO_6$ at 5 K. Bars stand for allowed reflections of the analyzed phases. First row corresponds to the main $NaPrFeWO_6$ phase while 2nd and 3rd rows correspond to $NaPrWO_4$ and $Na_2WO_4.2(H_2O)$ impurities, respectively. (b) Crystal and magnetic structure of $NaPrFeWO_6$ at 5 K.

The refinement of the magnetic modes clearly shows that the magnetic moments of Pr^{3+} and Fe^{2+} are collinearly oriented along the [0, 1, 0] direction giving rise to ↑↑↓↓ Pr zig-zag chains (↑·↓· for Fe) of M_y magnetic moments running along a-axis (see Fig. 3-b). The refined magnetic moments for Pr^{3+} and Fe^{2+} atoms at 2 K are 0.73(4) μ_B and 1.90(2) μ_B, respectively. The lack of full polarization of the magnetic moments in the ground state reveals the presence of magnetic frustration in the system. Further details about the neutron analysis and macroscopic properties for this sample can be found in the full study [1].

References.

[1] J. Blasco et al. Acta Materialia 176 (2019) 53-62
[2] A. M. Glazer Acta Cryst. A 31 (1975) 756-762.
[3] M. Retuerto et al., Inorg. Chem. 52 (2013) 12482-12491.
[4] B. J. Campbell et al., J. Appl. Crystallogr. 39 (2006) 607-614; available at ISOTROPY Software Suite, iso.byu.edu.