Experimental Report

Proposal: **5-31-2270** **Council:** 10/2012

Title: Magnetic structure determination of PrMn7O12 polymorphs

This proposal is a new proposal

Researh Area: Physics

Main proposer: **PRODI ANDREA**

Experimental Team: PRODI ANDREA

Local Contact: RITTER Clemens

Samples: PrMn7O12 monoclinic
PrMn7O12 rhombohedric

Instrument	Req. Days	All. Days	From	To
D1B	0	1	28/03/2013	29/03/2013
D2B	4	2	26/07/2013	28/07/2013

Abstract:

The AA'$_3$Mn$_4$O$_{12}$ family of manganites with quadruple perovskite structure has recently attracted a lot of interest as a disorder-free model system for many of the phenomena usually sought after in doped manganites, such as charge, orbital and spin ordering phenomena and multiferroicity. Indeed, their unique crystal framework allows to control the valence state of the Mn in octahedral coordination by full chemical substitution on the A site without introducing chemical disorder. Within this family of metastable compounds, PrMn$_7$O$_{12}$ is the only known phase to crystallizes in two different forms with rhombohedral and monoclinic symmetry depending on the synthesis conditions. Although the two forms differ slightly from the crystallographic point of view, their magnetic behavior as observed from bulk magnetization is dramatically different.

A detailed investigation of the magnetic structure by means of high-resolution neutron diffraction is therefore needed in order to characterize the ground state of these intriguing phases.

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The original proposal concerned the study of the low-temperature magnetic structure of $PrMn_7O_{12}$ polymorphs, but due to issues in shipping active samples from another neutron facility where preliminary studies had been carried on, the experiment at ILL focused instead on the related $Pb_2Mn_{0.5}Co_{0.5}WO_6$ (PMCW) double perovskite system.

In the frame of multifunctional materials the lead based double perovskite are recognise as peculiar systems showing unusual features. In particular in the scenario of the multiferroics material they play an interesting rule on the understanding the interplay between lattice distortion, due to the asymmetric coordination polyhedral of Pb^{2+}, and magnetism.

In this experiment we study the nuclear and magnetic structure of $Pb_2Mn_{0.5}Co_{0.5}WO_6$ (PMCW) double perovskite. This system present two magnetic transition, the first one around 180K and a second one around 10K, from the fit of the paramagnetic region was obtained a negative $\Theta_{C\text{-}W}$ indicating that the major exchange contribution is antiferromagnetic. From the electrical point of view the system is insulating with high dielectric constant and a transition between the paraelectric phase and the ordered one around 350K.

The neutron diffraction data was taken at the ILL institute at the beam line D2B and D1B. Almost 3g of powder sample was put in a vanadium can and the diffraction pattern were collected in the temperature range between 430K and 2K on cooling at D1B and between 500K and 2K on warming at the D2B beam line. The nuclear Rietveld refinement was conducted with the GSAS and EXGUI software. As expected at high temperature the nuclear structure is a cubic paraelectric double perovskite with s.g. Fm-3m. The Rietveld refinement of the D2B data obtained at 500K are show in figure 1a. The system didn't show anti-site defect on the B site and the refined occupancy of the B site was 52% Mn and 48% Co.

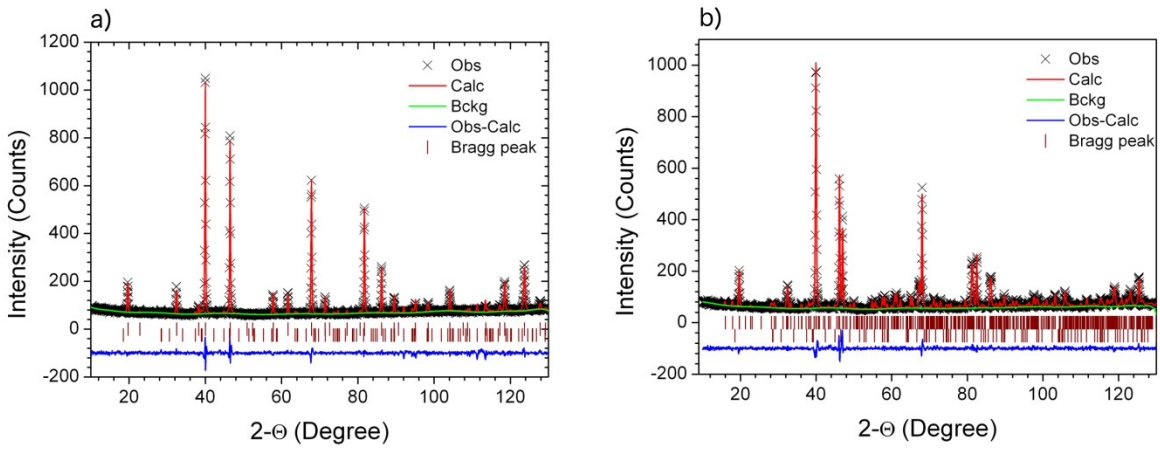

Figure Rietveld refinement of the PMCW sample: a) cubic phase at 500K (R_p=4.6% Rwp=6.14%) and b) orthorhombic phase at RT (R_p=5.2% Rwp=6.5%). The lower tick mark indicate the spurious phase PbWO4

With the decreasing of temperature the system undergoes to a phase transition to an orthorhombic electrical ordered phase. The orthorhombic structure is closely related to the one of the Pb_2MnWO_6 (PMW) compound. The orthorhombic superstructure is connected to the primitive perovskite by the relation $b \approx 2a_p$, $c \approx \sqrt{2}a_p$ $a \approx 2\sqrt{2}a_p$. The refinement was carried out with two space groups $Pmc2_1$ and Pmcn. The first one is the non-centrosymmetric s.g. characteristic of the PMW structure (obtained from single crystal measurement), the second one is the characteristic centrosymmetric space group proposed in literature for this double perovskites superstructure. The two refinements give very close reliability factor so we choose the centrosymmetric Pmcn and the RT refinement is shown in figure 1b. Around 100K the system undergoes to another phase transition to a monoclinic phase but at the moment the s.g and the nuclear structure is still missing. As shown by the volume vs. temperature graph in figure 2 this transition presents a thermal hysteresis and seems to have a fist order character. Regarding the high temperature transition, in a short temperature range, is evident the coexistent of the orthorhombic and cubic phase.

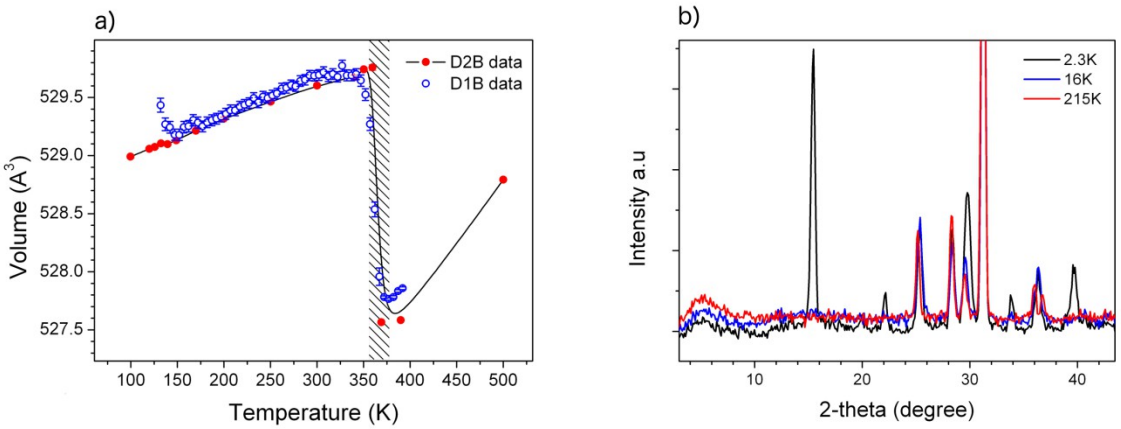

Figure a) Thermal evolution of the cell volume versus temperature, D1B data on cooling D2B on warming from 2K. Below 100K there is the unknown monoclinic phase. B) Comparison between the 2.3, 16 and 215K diffraction pattern obtained at the D1B line, are evident new magnetic diffraction peak in the 2K pattern and a diffuse scattering in the 16K one. For evaluation in shown also the 215K pattern, taken above the first magnetic transition.

Regarding the magnetic part, below 10K there is the rise of extra magnetic reflection probably related to the second magnetic transition observed in the magnetization measurement (figure 2b). Unfortunately the lack of the low temperature nuclear structure do not allowed solving the magnetic structure. Below the first magnetic transition there isn't evidence of magnetic contribution to the diffraction pattern but only the presence of small diffuse scattering and a reduction of the paramagnetic background as shown in figure 2b.

In order to solve the low-temperature crystallographic structure and, on the basis of this result, the magnetic structure, high-resolution synchrotron X-ray powder diffraction experiments are scheduled in spring 2014 at ESRF.