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ESRF

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- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Magneto-elastic coupling in the two-dimensional triangular lattice $NaMnO_2$	**Experiment number**: HS-3622
Beamline: ID31	**Date of experiment**: from: 14/05/08 to: 17/05/08	**Date of report**:
Shifts: 6	**Local contact(s)**: Irene Margiolaki	*Received at ESRF:*

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Report:

The AMO_2 (A= H, Li, Na; M= 3d transition metal) compounds have been the subject of many investigations in the last 20 years due to their potential application as intermediate electrodes in rechargeable Li batteries. In the last few years, these systems have also attracted considerable interest from experimentalists and theorists in physics because of the two-dimensional (2D) triangular lattice geometry. Here, the transition-metal ions are located at the center of edge-sharing O octahedra, forming a lattice of regular or isoscele triangles (depending on M), which map into the well-known 2D triangular lattice (Fig. 1a). Among all compounds of the series, $NaMnO_2$ is particularly interesting because the electronic configuration promotes an active Jahn-Teller state and the crystal structure shows that orbital ordering of the Mn^{3+}-dz^2 orbitals is already present at room temperature. This strong anisotropy and possible coupling between spin and orbital ordering on a triangular lattice, is uncommon and worth to be investigated. Our previously performed neutron powder diffraction (NPD) data revealed clearly an antiferromagnetic (AFM) ordering within the Mn-triangular lattice despite the prediction of a disordered ground state and Rietveld refinement had shown a unique solution for the magnetic structure [1]. The determined magnetic configuration (consists of AFM Mn-chains along the *b*-axis, stacked ferromagnetically and antiferromagnetically along the other two triangular directions) leads to an exact cancellation of the nearest-neighbor exchange energy and seems to be associated with a structural distortion to a triclinic cell. To gain further insights into the physics of this system, we studied the evolution of the crystal structure of α-$NaMnO_2$ in the ID31 beamline. In particular, we aimed to study the low temperature structural transition associated with the 3D magnetic ordering (T_N= 45 K) and prove the triclinic distortion, which has been proposed from NPD studies. In addition, probing the evolution of the anisotropic strains is crucial to understand the evolution of 2D magnetic ordering and the magneto-elastic properties of this compound.

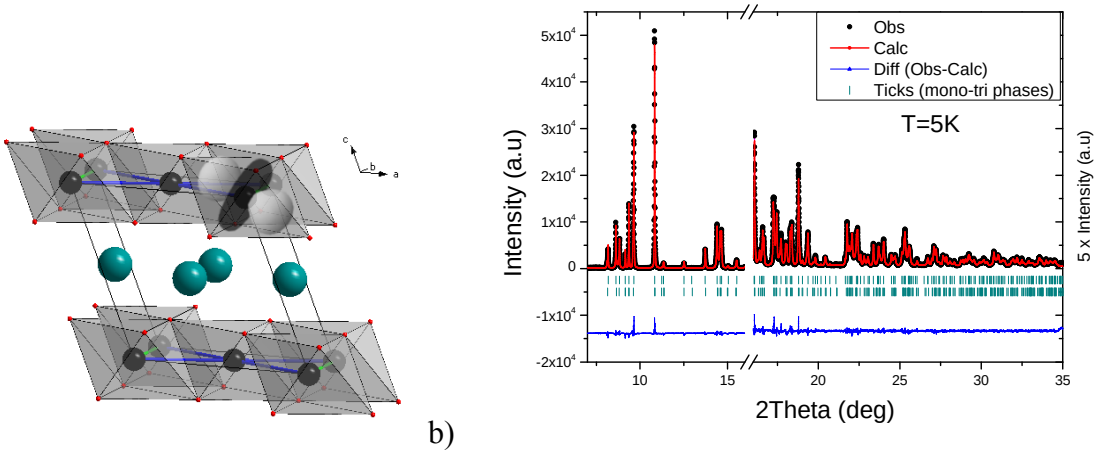
Six (6) shifts were allocated to our porposal for studying α-$NaMnO_2$ on the ID31 beamline (λ= 0.39986 Å) as function of temperature. To avoid sample deterioration, powders were sealed in borosilicate

glass capillaries under inert atmosphere in a glove-box. High statistics data were collected at selected temperatures, nominally at 5, 30, 60, 100, 200 and 295 K. Intermediate lower statistics scans were performed every 20 K from base and up to room temperature. Additional patterns were collected on cooling and heating from 5 K to 125 K, with temperature steps of 5 K. For the latter, we inserted a small amount of Si powder together with the sample in the capillaries for the purpose of having a better temperature reference. At a second stage, the He-cryostat was replaced by the hot-air blower to study the structure evolution above room temperature, i.e. at 100, 300, 500, 650°C.

Preliminary Rietveld refinements were performed on the high statistics datasets and are described below. The data were initially modeled at high temperature in the monoclinic phase, C2/m space group (χ^2: 11.9; R_F-factor: 4.35%). After various tests, we realised that the low-T behaviour could be better modeled by two coexisting phases, a monoclinic and a triclinic one (Fig. 1b). We argue that this latter phase originates from a symmetry lowering necessary to lift the magnetic frustration and capable of leading to the observed AFM long-range order (LRO) by NPD [1]. Rietveld refinements of the ID31 data with either the monoclinic or the triclinic phase only do not model properly the low-T data (pertain into significant anisotropic peak broadening) leading to poor agreement factors (χ^2: 10.4; R_F-factor: 2.95% and χ^2: 10.7, R_F-factor: 2.64% for the monoclinic only and triclinic only phases, respectively).

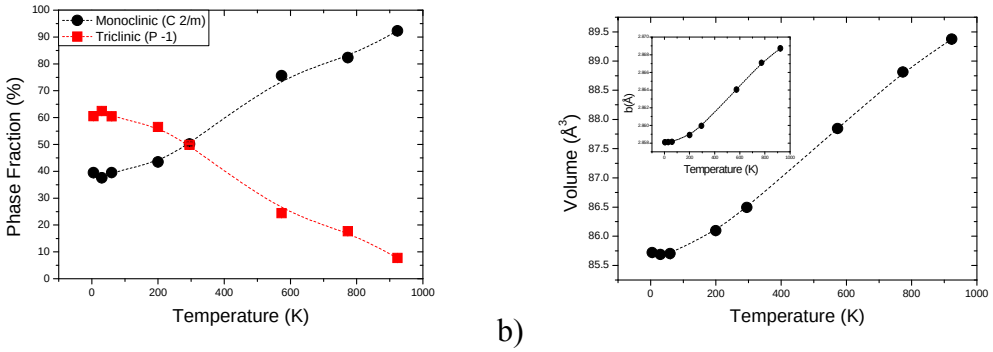
The low-T data do not show any appreciable peak splitting to confirm a clear transition to the triclinic space group symmetry (P-1). However, evidence for the inadequacy of the monoclinic symmetry is offered through observable hk0 anisotropic peak broadening (Fig. 3a). In addition, peak shape asymmetries probably due to defects, such as stacking faults, can also play a role in the not perfect description of the powder pattern. Due the almost 2D structure of the AMO_2-type compounds, this kind of defect is likely and rather difficult to take into account during the present stage of the data analysis. The use of anisotropic microstrain parameters, based on the Stephen's formulation (S_{HKL}), significantly improved the single-phase refinements in the whole temperature range. However, even this apporach on its own at low temperature, is not sufficient to account for the large peaks anisotropies observed. We therefore included a second phase, in the triclinic symmetry, attributing it into the the large magneto-elastic coupling for the relief of the strong magnetic frustration in the triangular lattice. This approach resulted in improved overall refinements (χ^2: 4.83; R_F -factor: 2.21% and 2.13% for the monoclinic and triclinic phase, respectively). The volume fractions of the two coexisting microscopic domains have been Rietveld refined up to about 950 K (Fig. 2a); they show a large change from about 40% for the (frustrated) monoclinic phase at 5 K up to about 90% at 950 K. Below T_N we also observed negative lattice thermal expansion both in the *a*, *c* (and *beta*) parameters, while the *b* lattice size remains almost constant below that temperature (Fig 2b). In Fig. 3b, large strains in the monoclinic symmetry are observable in the planes perpendicular to the *b*-direction. Namely, S_{HKL} parameters with non-zero H component are larger and increase upon cooling and especially while one approaches the T_N. This behaviour is an important indication that some disorder must take place along the in-plane stacking sequence of the AFM Mn-chains.

It is worth noting that the results described above are preliminary and due to the lack of observable peak splitting as well as the presence of large peak asymmetries, the performed refinements could only give an indication of structural anomalies in the low temperature regime and in particular around T_N. The microscopic picture of coexisting domains could indicate the presence of competing 2D (frustrated) and 3D (LRO) spin correlations, with the latter to establish a dominant (triclinic) phase at low temperature. Due to the afore-mentioned structural disorder effects that introduce correlations in the strain as well as in the other two-phase parameters, the proposed model represents a plausible approach to the ID31 data that would require further validation.



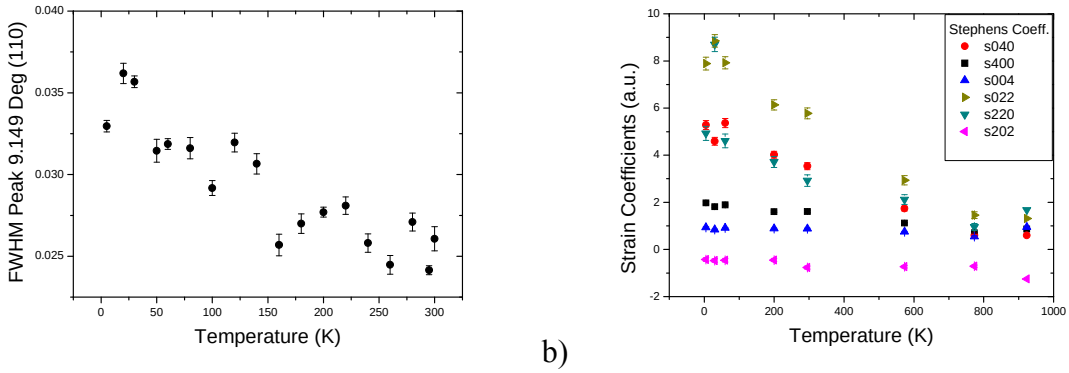
a) b)

Figure 1. (a) Nuclear structure of the $NaMnO_2$ in the monoclinic symmetry(from data collected at 200 K). (b) Two-phase Rietveld refinement of the T= 5 K high statistics dataset. The plots in the 2θ= 16-35° have been multiplied by 5.



a) b)

Figure 2. (a) The volume fractions of the two phases as function of temperature.; *squares* respresent triclinic microscopic domains and *circles* represent the monoclinic ones. (b)Temperature dependence of the volume of the monoclinic phase, inset: T-dependence of the monoclinic *b*-lattice parameter. The lines are guide to the eye.



a) b)

Figure 3. (a) Temperature dependence of the FWHM of the (110) Bragg reflection (monclinic setting), showing characterisic peak while approaching the T_N. (b) The Stephen's microstrain parameters S_{HKL} as function of temperature in the monoclinic phase.

References

[1] M. Giot, L.C. Chapon, J. Androulakis, M. A. Green, P.G. Radaelli, and A. Lappas, *Phys. Rev. Lett.* **99**, 247211 (2007).