ESRF	**Experiment title:** Charge, orbital and spin study of the mixed valence manganite NaMn7O12 by Resonant X-ray Scattering.	**Experiment number**: HE2166
Beamline: ID20	**Date of experiment**: from: 21/06/2006 to: 27/06/2006	**Date of report**: 25/11/2006
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Report:

The double perovksite (NaMn$_3$)Mn$_4$O$_{12}$ [1-3] has recently attracted considerable interest because of the structural analogies with half-doped manganites and the same mixed-valence state is realized in the absence of chemical disorder. It undergoes a structural transition accompanied by charge ordering at T_{CO}=176K, followed by the antiferromagnetic ordering of the Mn spins in the octahedral sites at T=125K and of those belonging to the A' sublattice at T=90K. The observation at 125K of the spin-charge ordering pattern of C-E-type strongly supports the analogy with the physics of half-doped manganites.

In the experiment HE2166 performed at the magnetic scattering beamline ID20 we examined a NaMn$_7$O$_{12}$ single crystal (350 x 500 x 700 μm) of very good crystalline quality (FWHM of 44 arcsec), obtained from the quench of a HP synthesis experiment [3]. The experiment was performed in vertical scattering geometry and with incident linear polarisation.

We first investigated the cubic-to-monoclinic structural transition (sg Im-3 to I2/m) occurring at $T_{CO} = 176$ K.

We characterized the temperature dependence of the order parameter by monitoring the splitting of the (440) reflection and detected the superlattice (SL) peaks associated with the long range cooperative Jahn-Teller distortion accompanying the transition, previously observed only in high-resolution powder diffraction experiment [2]. After a survey of the accessible reciprocal space we were able to confirm that the structural modulation has a propagation vector $\mathbf{k} = (1/2,0,-1/2)$, so that each SL position receives contributions from two different satellites, hence the asymmetry in intensity of the SL peaks seen in Fig 1.

Upon tuning the photon energy through the absorption edge of Mn we could observe a large resonant enhancement. Using a Cu 220 analyser crystal we have then performed the polarisation analysis at the charge ordering peaks, selecting out the $\sigma\sigma$ and $\sigma\pi$ channels.

During the allocated time we were able to complete the azimuthal scan of two SL reflections.

Some representative spectra are shown in Fig 2 for the (3.5 1 3.5) reflection for two different azimuth angles. Two features are evident in the $\sigma\pi$ channels at 6.550 KeV and 6.558 KeV, respectively.

In analogy to what established in the literature for manganites with simple perovskite structure, we interpret the first resonant feature as being dipolar in origin, perhaps suggesting that hard x-rays are more sensitive to the JT distortion then to the peculiar d orbital occupation.

The second resonance to our knowledge has never been observed before in manganites and represents the most interesting result obtained in the experiment. We can exclude the hypothesis of multiple scattering since we have observed it at several charge ordering reflections, corresponding to different azimuthal projections. We speculate it could be associated to only one type of distorted MnO_6 octahedra and represent the signature of the full charge disproportionation in this system. In support of this hypothesis a recent RXS study of magnetite [4] reported a similar double structure separated in energy by a few eV, which they could account for with a model of modest charge disproportionation on inequivalente Fe sites. Alternatively, it could be related to the Mn^{3+} ion on the A' sublattice and to its unique rhombic prism coordination, whose electronic configuration has not being investigated yet. In order to validate the above hypotheses, ab initio calculations of the structure factors at resonance to relate such models with experimental data are currently under way.

Work is planned in the future to extend the analysis to a larger set of reflections, to explore the effects of applied magnetic fields and to continue the study to the soft x-ray regime and to other members of the $AA'_3Mn_4O_{12}$ series with different Mn mixed-valence state.

References:

[1] B.Bochu *et al.*, J. of Solid State Chem. **11**, 88 (1974).
[2] A. Prodi *et al.*, Nat. Mater. 3, 48 (2004).
[3] E. Gilioli et al., Journal of Crystal Growth, v 275, n 1-2, 15 Feb. 2005, p e877-80
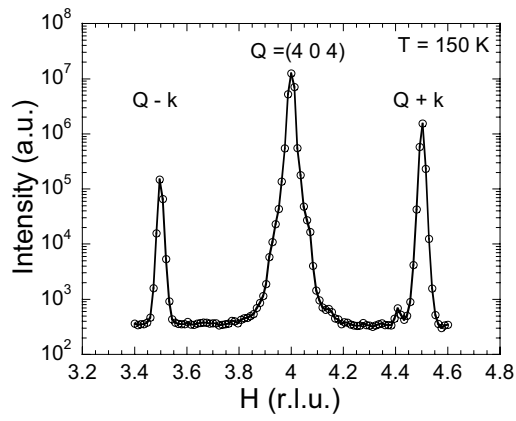[4] E. Nazarenko *et al.*, Phys. Rev. Lett. 97, 056403 (2006).

Fig. 1 Reciprocal lattice scan of satellite reflections associated with charge ordering in $(NaMn_3)Mn_4O_{12}$

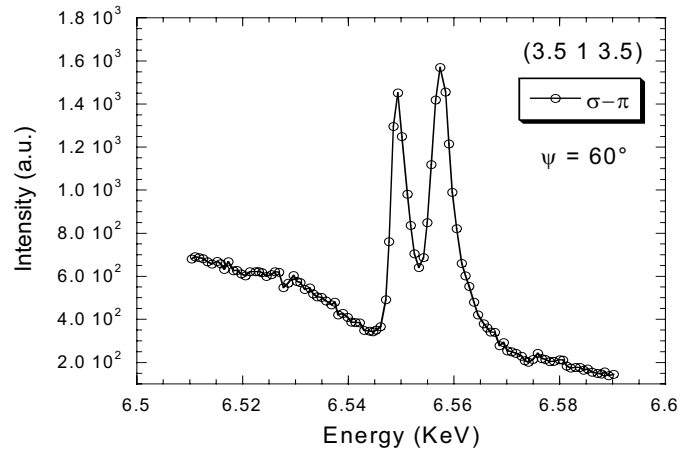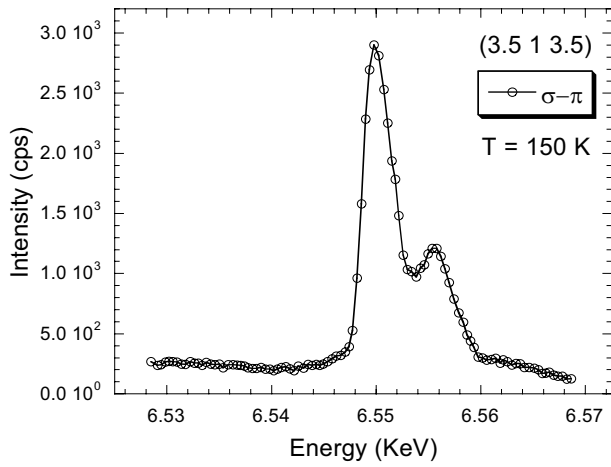FIG. 2 Experimental resonant X-ray diffraction peak spectra of $NaMn_7O_{12}$ at T=150K taken at two different azimuth angles. Experimental data have not been corrected for absorption