ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- 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:** Phonon spectroscopy and the Verway transition in $NaMn_7O_{12}$	**Experiment number**: HC1405
Beamline:	**Date of experiment**: from: 5/3/14 to: 11/3/14	**Date of report**: 21/3/14
Shifts:	**Local contact(s)**: Alexei Bosak	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Luigi Paolasini*, ESRF

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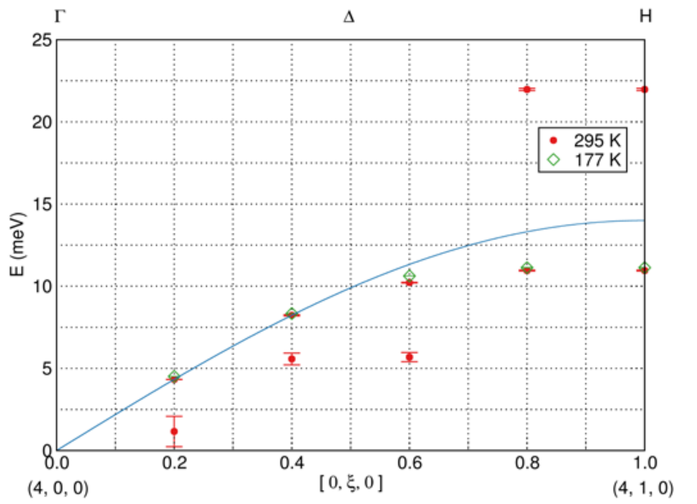
Report:

IXS experiment on $NaMn_7O_{12}$ was performed at ID28 with the spectrometer setting with Si(9,9,9) reflection of the backscattering monochromator, leading to photon energy E = 17.794 keV and energy resolution of δ E=3.2 meV. Machine mode was 16 bunches.

Sample was etched to a needle shape like crystal that was reglued on a capillary to have the (HK0) with respect to the cubic HT phase on the scattering plane. The sample temperature was changed with a LN cryostream. The measured Q points at various temperature T>150K were measured around τ =(400), τ =(440) and τ =(600).



First, a survey of the reciprocal scattering at 295K was performed to explore the features of the major phonon branches, since the present was the first phonon spectroscopy experiment on $NaMn_7O_{12}$.

In transverse scans, shown in Fig.1, the dispersion of strongest acoustic mode clearly deviates from sinusoidal behavior for ξ >0.4 . Physical explanation may include a flattening of transverse Δ_3 acoustic mode at H, a softening of the mode from halfway and up to the zone boundary (ZB), like SmS under pressure or signature of electron-phonon interactions. Support of *ab initio* phonon calculations is needed for further speculations, given the large number of atoms in the unit cell.

The speed of sound, roughly estimated from first q point, is v_s ~ 3812 m/s.

One goal of the experiment was to investigate with IXS the nature of the “Butterfly pattern” features observed below the charge-ordering transition from diffuse scattering in diffraction experiments, in analogy to recent experimental observations for the Verway transition in magnetite.

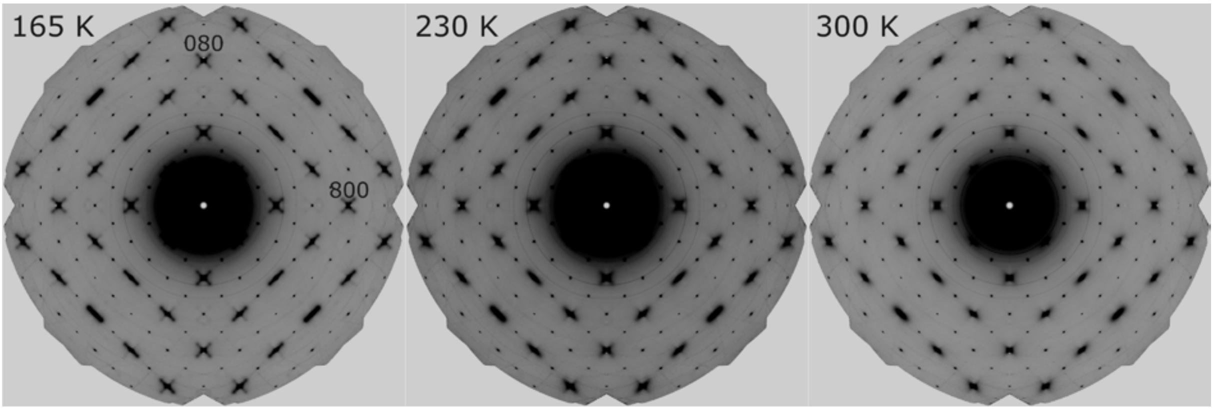
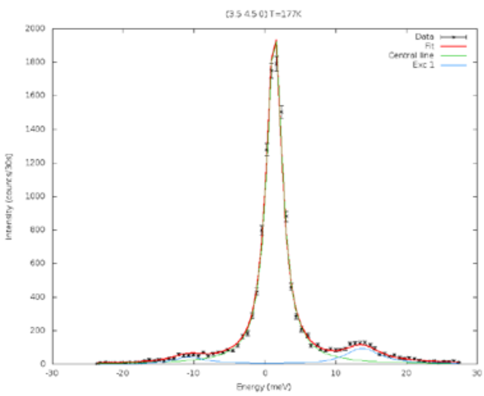
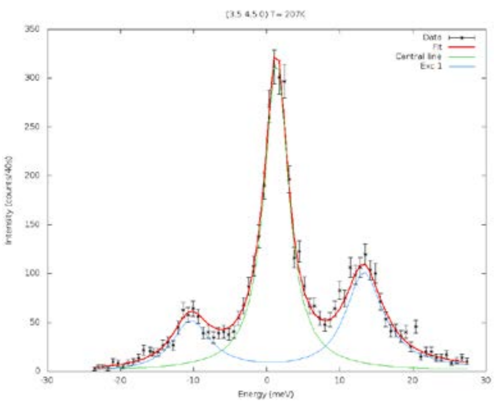


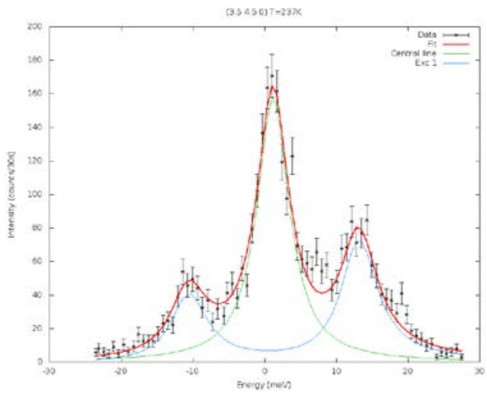
Fig. 2. Temperature dependence of HK0 reciprocal space cuts of $NaMn_7O_{12}$ (taken at **BM01A).**

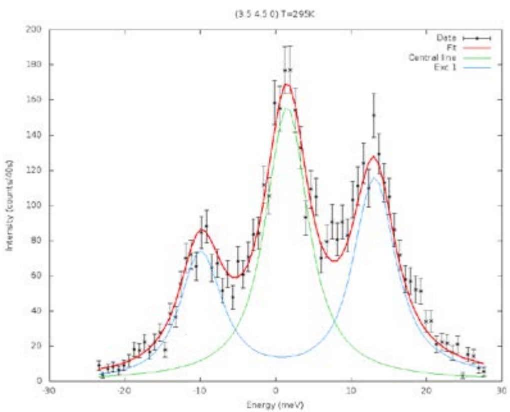
To this end, scans along (4-ζ,4+ζ,0) were performed at selected temperatures, at T=177K, right above the transition, at 207K, 237K, 267K, and 295K.

The quasielastic line was extracted from fits to the first acoustic mode, without convoluting to the resolution function. For (3.9 4.1 0) the fitting strategy is more problematic due to the severe overlap between acoustic and quasielastic mode, making an unconstrained fit of relative intensity weight not meaningful; shown is the fit where all the excitation parameters (energy and intensity) were constrained.









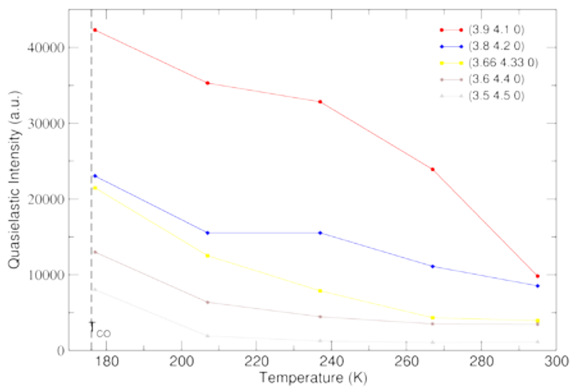


Fig. 3. Quasielastic scattering observed by IXS above the charge-ordering transition, scans are for (3.5,4.5,0).

Results show that the correlations originating in the microscopic distortions accomodating the charge-ordering pattern below T_{CO}, which appear as a “butterfly” feature in diffuse scattering, do survive as quasielastic scattering well above the charge-ordering transition and up to room temperature, probably a signature of the underlying polaronic dynamics.

Scans along (6+ζ,0,0) and (6+ζ,ζ,0) were collected first at room temperature with high statistics at 150sec/pt to characterize the optical phonon excitations, shown in Fig.4.

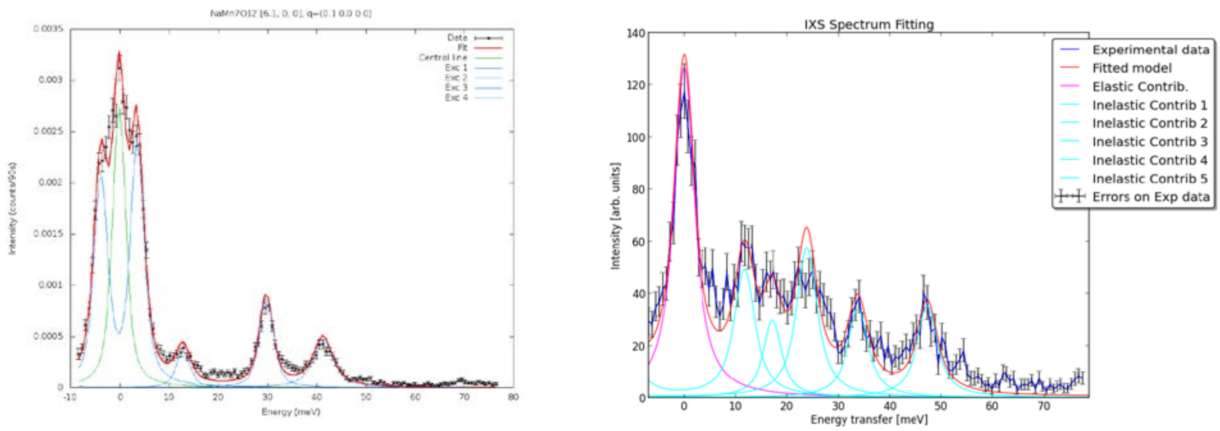


Fig. 4. Optical phonons observed by IXS at room temperature, scans are for (6.1,0,0) (left) and (6.5,0.5,0) (right), respectively.

In the (6.1,0,0) three modes E_1=13.4 mev, E_2=30.2 mev and E_3=41.2 mev are clearly distinguishable and optical modes energies are compatible with what previously observed in IR spectroscopy at 102 cm^{-1}, 240 cm^{-1} and 320 cm^{-1}, respectively (Lupi et al. umpublished), while at (6.5,0.5,0) several more modes are excited and the extraction of mode frequencies is less reliable.

Finally, to investigate possible phonon softening across the Verway transition at q_{dc}=(½ 0 ½) , high statistics scans were collected at temperature just above the phase transition. No sign of softening has been observed for the acoustic branch at (3.5,4.5,0). Fig. 5 shows the comparison of (6.5,0.5,0) scans at RT and 177K, which does not provide concluding evidence regarding the possible softening of optical modes. More experiments are needed to probe different zones in order to clarify this important aspect of the Verway transition in $NaMn_7O_{12}$.

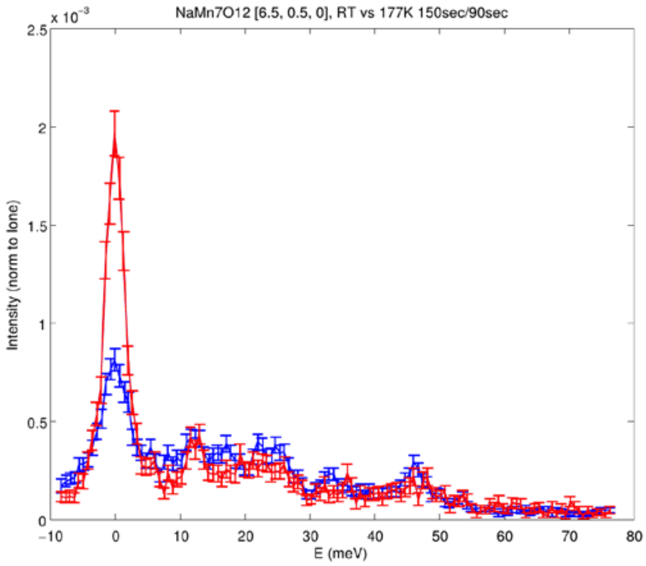


Fig. 5. Optical phonons observed at (6.5,0.5,0) at room temperature and T=177K, respectively.