



	<b>Experiment title:</b> Study of the anomalous Jahn-Teller dynamics at the Verwey transition in $\text{NaMn}_7\text{O}_{12}$	<b>Experiment number:</b> HC-2499
<b>Beamline:</b> ID28	<b>Date of experiment:</b> from: 08/06/16 to: 14/06/16	<b>Date of report:</b> 02/08/18
<b>Shifts: 18</b>	<b>Local contact(s):</b> Alexei Bosak	<i>Received at ESRF:</i>
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## Report:

The objective of the present experiment was to unveil the phonon signature of the Jahn-Teller distortion of the  $\text{MnO}_6$  octahedra occurring at  $T_{\text{CO}}=175$  K in the cubic  $\text{Im}\bar{3}$  structure of the quadruple perovskite  $\text{NaMn}_7\text{O}_{12}$ . This distortion stabilizes a commensurate  $\text{I}2/m$  monoclinic structural modulation with propagation vector  $\mathbf{q}_{\text{CO}}=(-\frac{1}{2} \frac{1}{2} 0)$  and an almost ideal  $\text{Mn}^{3+}/\text{Mn}^{4+}$  charge-order.

In order to reach this objective, we have taken a series of IXS spectra at room temperature and at 175 K along the cubic [110] direction crossing  $\mathbf{q}_{\text{CO}}$  on an approximately cubic-shaped  $\sim 100$   $\mu\text{m}$  single crystal. The above sample size was chosen to optimize the signal in transmission geometry by orienting the sample with the [100] direction parallel to the incoming photon beam and the [001] direction perpendicular to the scattering plane.

As to the energy of the photons beam used (in 16-bunch mode), the Si(999) line of the monochromator was chosen as a compromise between the opposite requirement of high energy resolution and of high signal-to-noise ratio, considering that a good statistics was required to reliably determine the energy of the optical phonons in the high-energy region of the spectrum where the structure factor rapidly decreases.

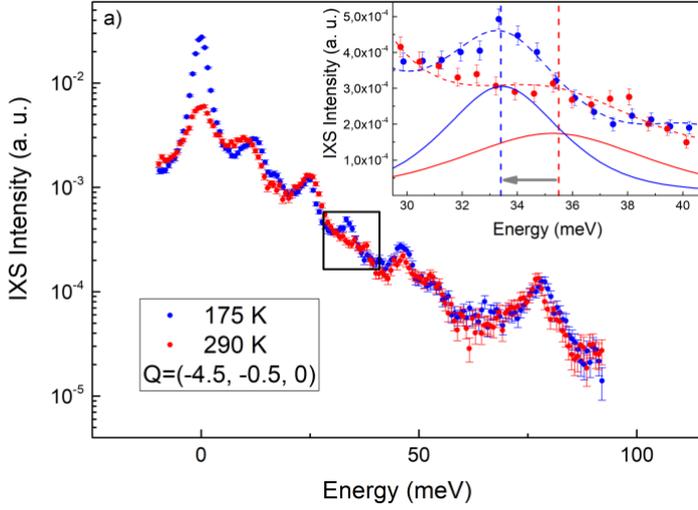
Using the above experimental conditions, we sampled wave vectors  $\mathbf{Q}=(4-\xi, -\xi, 0)$ , near the (400) Bragg peak where the structure factor is largest, for  $\xi=0.3, 0.4$  and  $0.5$  in an extended region from  $-10$  to  $90$  meV of transferred energy enabling to probe all phonons. Note that, at 175 K, we probed the thermodynamic fluctuations of the CO transition. Well inside the CO phase below  $T_{\text{CO}}=175$  K, the twin domain structure stable in the distorted monoclinic phase would have mixed the phonon dispersion along different crystallographic directions.

In order to determine precisely  $T_{\text{CO}}$ , we used a cryostream and a CCD camera to control the sample temperature and to monitor in real time the cubic-to-monoclinic distortion by detecting the satellite diffraction peaks of the commensurate modulated structure. We checked the reproducibility of the  $T_{\text{CO}}$  measurement by lowering the cooling rate until the point where no hysteresis in the temperature dependence of the diffraction pattern was detected.

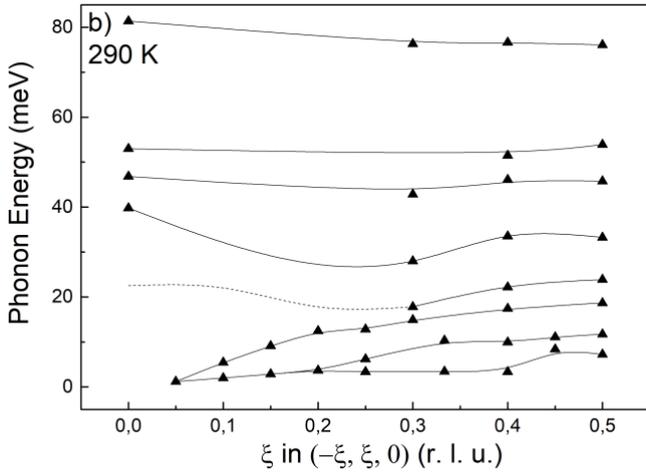
The position and width of each individual phonon modes were determined by fitting the whole IXS spectra in the above  $-10$  to  $90$  meV range by using pseudo-Voigt peak functions. The zero-energy position of the elastic peak was determined by imposing the usual Bose-factor constraint on the position and intensity of the Stokes and anti-Stokes peaks of the first acoustic phonon.

In spite of the limitation of probing at  $T_{CO}$  only the thermodynamic fluctuations of the order parameter of the CO phase, we could unambiguously detect a clear  $\sim 2$  meV phonon softening of the  $\sim 31$  meV mode in the 175 K data for  $\xi=0.5$ , *i.e.* exactly at the  $\mathbf{q}_{CO}$  wave vector where an anomalous lattice dynamics was expected (see Fig. 1). By analyzing the signal of all the additional detectors of the detector bank, we could explore nearby reciprocal wave vectors shown in Fig. 2c, which confirmed the existence of a pronounced mode softening at  $\mathbf{q}_{CO}$  (see Fig. 2b). A confirmation of the existence of an anomalous lattice dynamics at 175 K is given by the analysis of the width of the quasi-elastic peak, which also displays an anomalous broadening at complementary at the above temperature at  $\mathbf{q}_{CO}$ . A comparison of the dispersion relationship at 175 K with that at room temperature (see Fig. 3) shows that the softening is present only in the former case, which clearly indicated that the softening reflects the incipient CO transition.

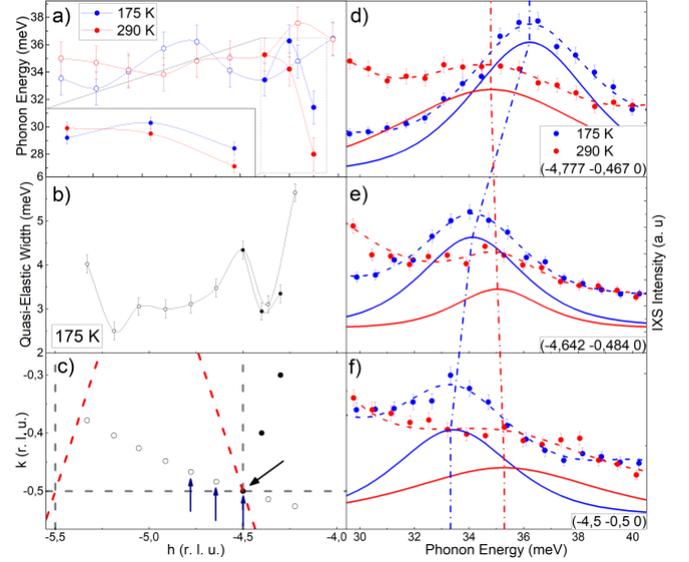
In a publication in preparation, complementary first-principles phonon calculations should allow us to identify the symmetry of the soft mode, thus providing a physical interpretation of the driving force of the CO transition.



**Figure 1.** Representative IXS spectra for  $\mathbf{Q} = (-4.5, -0.5, 0) = \mathbf{G}_{-400} + \mathbf{q}_{CO}$  taken at 295 K and at  $T_{CO}=175$  K. Note the 2 meV softening of the mode at 31 meV in the 175 K spectrum at the verge of the CO transition. Upper inset: close-up of the spectra in the energy region where the softening is observed. According to first-principles calculations, the symmetry attributed to this mode is  $T_g$ .



**Figure 3.** Experimental IXS (black triangles) and calculated (solid line) [110] dispersion of both acoustic and optical modes at 290 K. The points at  $\Gamma$  are taken from Raman spectra.



**Figure 2. Panel a:** Energy dispersion of the  $T_g$  soft mode along the [110] direction (full symbols) and the diagonal direction shown in panel c (open symbols). Note that both directions cross the  $\mathbf{G}_{-400}=(-400)$  reciprocal vector. Full symbols refer to the main detector of the detector bank. Open symbols refer to the others detectors. Note the mode softening seen in both data sets by approaching the critical wave vector  $\mathbf{Q}^* = \mathbf{G}_{-400} + \mathbf{q}_{CO}$ .

**Panel b:** Width of the quasi-elastic peak as a function of wave vector at 175 K. Symbols are as above.

**Panel c:** points in the  $(hk0)$  reciprocal plane at which the energy of the  $T_g$  soft mode in panel a and the width of the quasi-elastic peak data of panel b have been measured. Dashed lines indicate the Brillouin zone boundary of the cubic (red) and monoclinic (gray) unit cells.

**Panels d-f:** close-up of the IXS spectra taken at  $(-4.5, -0.5, 0)$ ,  $(-4.64, -0.48, 0)$  and  $(-4.78, -0.47, 0)$ , where the softening of the  $T_g$  phonon is observed. The position of these 3 points in the  $(hk0)$  reciprocal plane are indicated by arrows in panel c. Solid lines are a pseudo-Voigt fit of the soft mode, dashed lines are a fit of the whole spectrum including contribution of other modes (not shown). Dashed and dot lines show the evolution of the peak position.