EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

Experiment Report Form

	Experiment title: **Magnetoelastic coupling and insulator-metal transition in $TlNiO_3$ perovskite nickelate**	**Experiment number:** HC4990
Beamline: ID22	**Date of experiment:** from: 24/08/2022 to: 28/08/2022	**Date of report:** 27/09/2022
Shifts: 12	**Local contact(s):** Catherine Dejoie	*Received at ESRF:*

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Report:

In the provided beam time we started by a well-known perovskite, $HoNiO_3$, taken as a reference, for which we obtained excellent high-angular resolution patterns in ID22, working with a wavelength of λ= 0.35418 Å, measuring in the 2θ range up to 40º, with two 9 min acquisition per pattern. The sample was contained in a 0.4 mm glass capillary. **Fig. 1a** shows the Rietveld plot of $HoNiO_3$ at RT, with a inset showing the peak splitting between (224) and (-224) reflections, due to the charge disproportionation effect and the subtle monoclinic symmetry with β = 90.083(1)º. This sample was cooled down to 4 K and then warmed up while measuring up to RT, collecting diagrams every 9 min, in order to follow the thermal evolution of the crystal structure across T_N ~ 145 K [1]. Once established the experimental conditions, the $TlNiO_3$ sample was measured at 295 K and then cooled down to 4 K, following the same protocol. **Fig 1b** exhibits the quality of the fit at 295 K, in the monoclinic $P2_1/n$ space group. In this case, the monoclinic distortion is much weaker, and can be hardly distinguished, with β = 90.03(1)º, as described before from neutron diffraction data [2]. Nevertheless, the unique convergence of the atomic positions for the three distinct O atoms demonstrate that the internal symmetry is indeed monoclinic.

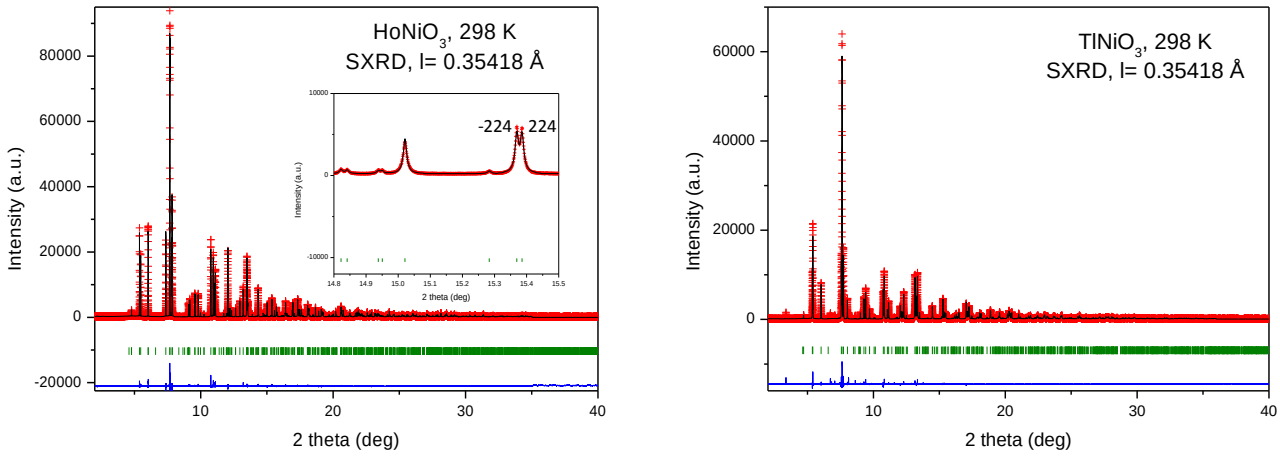

Fig. 1: Rietveld plots of **a** $HoNiO_3$ and **b** $TlNiO_3$ collected at RT at the high-resolution ID22 diffractometer. The inset illustrates the splitting of two characteristic reflections (-224) and (224) indicating the monoclinic symmetry of this material in the insulating regime, below the MI transition.

The low-temperature evolution of the unit cell parameters unveils strong magnetoelastic coupling when the structure evolves across the T_N, either for $HoNiO_3$ and $TlNiO_3$. Anomalous negative thermal expansion effects are observed for *b* lattice parameters, and the monoclinic beta angle experiences a non-monotonic behavior in the proximity of T_N. A publication to describe these effects is in progress. Beyond that, we have probed the unreported insulator-metal transition in $TlNiO_3$ using synchrotron X-ray diffraction. The results showed a clear sample decomposition for temperatures higher than 600 K; however, anomalies along the lattice parameters at the onset of the structural phase transition $P2_1/n \rightarrow Pbnm$ were detected. Such results are in agreement with our previous EXAFS investigation, as summarized below.

To provide additional information on the insulator-metal transition in $TlNiO_3$, we have probed the EXAFS data at high-temperatures. **Fig. 2a** shows the Fourier-transform EXAFS oscillations $|\chi(R)|$ under ambient pressure and at temperatures ranging from 300 and 550 K. Few temperature points from room temperature up to 625 K were used to investigate the insulator-metal transition, which is expected at T_{IM} ~ 600 K. The radial distribution can be divided in three parts: at 2 Å, 2.5–3.3 Å, and 3.6 Å, concerning the pairs Ni–O, Ni–Tl, and Ni–Ni, respectively. The pair-distances and their Debye-Waller exponents (the parallel MSRDs, $\langle u_{||}^2 \rangle$), as derived from the fitting, with a subtle increase at 550 K, see **Fig. 2b-c**. Above this temperature point, $TlNiO_3$ started to decompose and signals of NiO appeared in the XANES signal. Such a fact has direct connection with the metastable nature of Tl^{3+} ions within $TlNiO_3$ perovskite. Later XANES data were taken above 600 K and upon cooling down to room temperature, where only NiO features were observed in those signals.

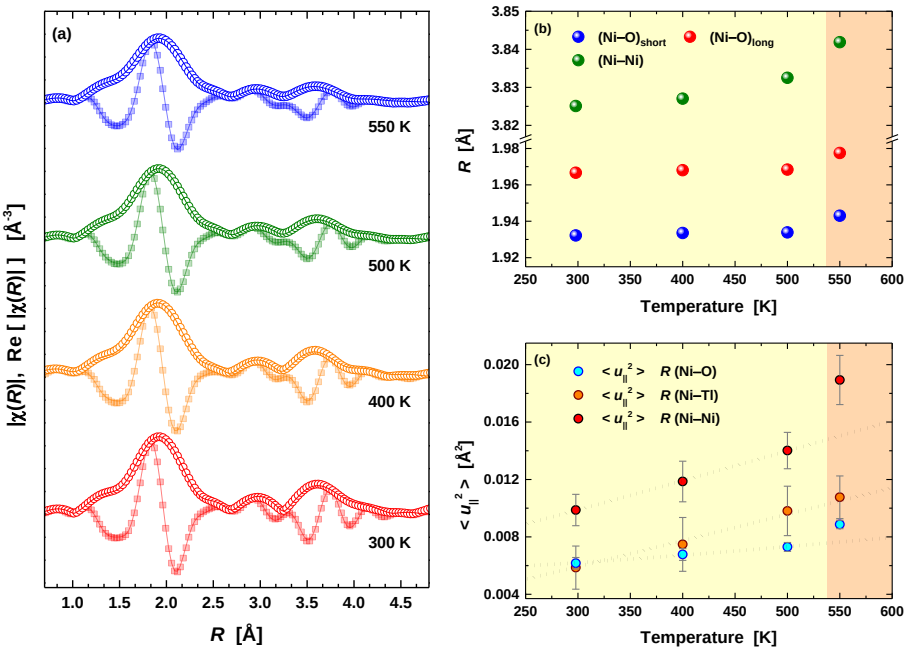

Fig. 2: Temperature-dependent EXAFS analysis at Ni *K*-edge: **a** Modulus and real part of the Fourier transform EXAFS oscillations $|\chi(R)|$ and $\mathrm{Re}[\chi(R)]$ in *R* space. The open symbols are the experimental data, while solid lines are the best fit adjusted. Temperature-dependence of **b** the path distances and **c** the Debye-Waller exponent.

References

[1] M. T. Fernandez-Dıaz et al, Phys. Rev. B64, 144417 (2001).

[2] S. J. Kim et al, Chem. Mater., 14, 4926-4932 (2002).