ESRF	Experiment title: **STUDY OF A NEW UNCONVENTIONAL PHASE IN THE STRONGLY CORRELATED OXIDES $RNiO_3$ (Y-Lu)**	**Experiment number**: **CH-1624**
Beamline: **ID31**	**Date of experiment**: from: **12/NOV/03** to: **14/NOV/03**	**Date of report**: **25/Feb/04**
Shifts: **6**	**Local contact(s)**: **Dr Irene MARGIOLAKI**	*Received at ESRF:*

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The observation of charge disproportionation (CD) in $YNiO_3$ is accompanied of a symmetry change from orthorhombic Pbnm to monoclinic $P2_1/n$. This proposal was aimed to explore and investigate the possibility of a subtle (weaker) second transition at $T_{CD}^{Glass} \approx$720-740K ($>T_{CD}^{3D}$=600 K) suggested by the resistivity, the susceptibility and the specific heat (C_p).

There was no problem with the beam and furnace (hot air stream). The full planned experiment was carried out. The main part of the beam time was used to collect data on $YNiO_3$ sample as a function of temperature. A minor part of the beam time was dedicated to other nickelates of the family $Nd_xA_xNiO_3$ pure of doped with divalent or tetravalent A cations.

A short wavelength, 0.429697(5) Å, was used to minimise the absorption and to extend the accesible Q-range in order to obtain more accurated oxygen positions and temperature factors. Capillar diameters ranging from ϕ=0.5 to 1.0 mm were used depending on the sample. The beam size on sample was 2.25x1.35 mm for measurements taken both at room or higher temperatures. For the latter, the working temperature was set using the hot air stream. Each SXRD run took about 45-60 minutes to have good statistics over the angular range 1 to 38º (2Θ). All patterns were collected with angular range and statistics suitable for a full structural Rietveld refinement, averaging several scans (3 scans in most of the cases, with tipically counting time of 15 min/scan.). The data from the detectors were normalized and summed to 0.003º step size. A RT run of Si NIST was performed for calibrations.

For $YNiO_3$ patterns were collected over the temperature range 294-920 K. The sample was very well crystallized in a single phase. Only very small traces (less than ~2 wt%) of NiO side phase was detected.

Several patterns were obtained between 294 and 600 K (charge-order monoclinic phase), across the monoclinic ($P2_1/n$) to orthorhombic (Pbnm) transition, and finally the possibility of a weaker changes in the orthorhombic phase was explored collecting data up to 920 K. The very high resolution of ID31 allowed to unambiguously resolve the monoclinic splitting of the charge-order phase (monoclinic β angle lower than 90.07).In Fig. 2 we compare the monoclinic (112)/(-112) doublet as observed in D2b, old BM16 and ID31 instruments at the same temperature. The thermal evolution of the two NiO_6 octahedra in the low temperature phase is shown in Fig. 3. Besides the strong transition at T~600 K, Fig. 4 suggests a tiny deviation in the evolution of the *b* parameter that coincides with a small anomaly in the specific heat. Full analysis of these data, including the evolution of line profile and joint refinement of neutron(d2b)%sincrotron (ID31) data will be reported elsewhere.

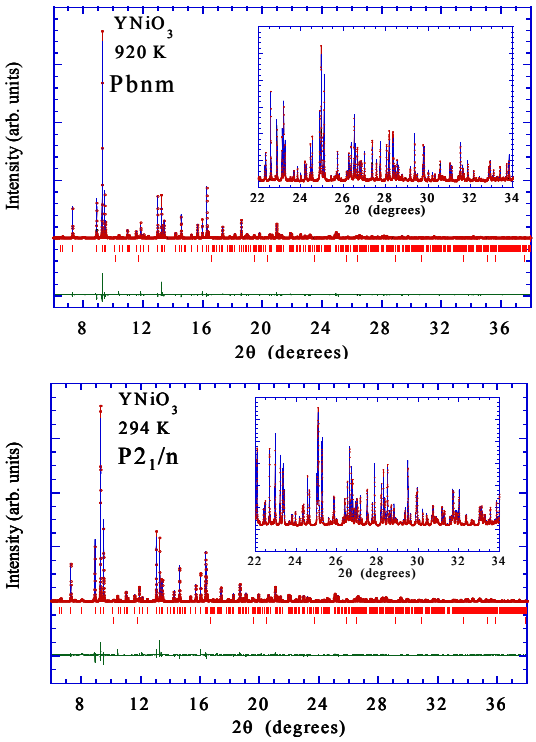

Fig.1: Refined pattern and detail of the high-angle range of $YNiO_3$ at RT and 920 K

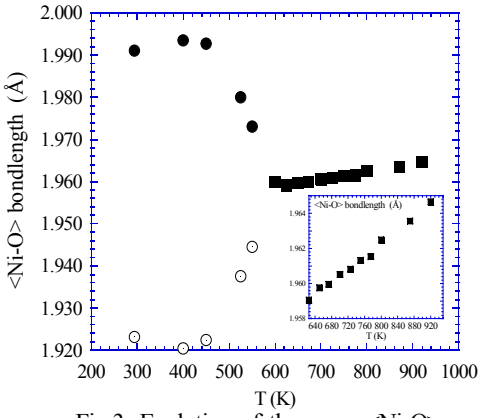

Fig.3: Evolution of the mean <Ni-O> distances in the NiO_6 octahedra.

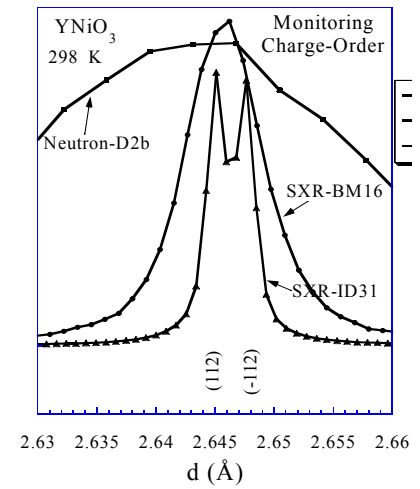

Fig.2: Comparison of the monoclinic splittting of (112)/(-112) reflections measured at RT using respectively D2B (neutrons), the old BM16 and ID31 beamlines. Monoclinic symmetry is the signature of CO in these oxides.

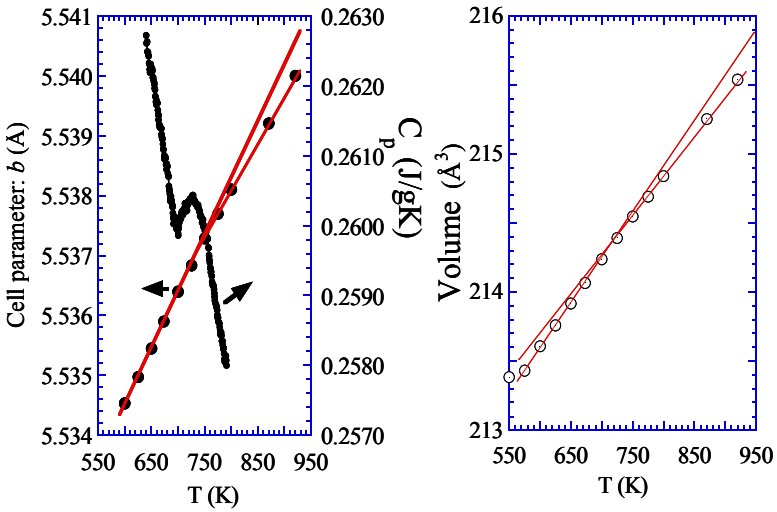

Fig.4: Evolution of the *b* parameter (and the volume) in the orthorhombic region. Comparison to that of the specific heat above 600 K.