ESRF	**Experiment title:** Temperature dependent structural changes in nickelates by resonant inelastic soft x-ray scattering	**Experiment number:** HE1545
Beamline: ID8	**Date of experiment:** from: 19.11.2003 to: 25.11.2003	**Date of report:** 1.03.05
Shifts: 18	**Local contact(s):** Dr. N.B. Brookes	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Marisa Medarde*, Jörg Voigt*: PSI (Switzerland)

Lucio Braicovich*, Claudia Dallera*, G. Ghiringhelli *, A. Piazzalunga*: Dipartimento di Fisica, Politecnico di Milano, Piazza Leonardo da Vinci 32, I-20133 Milano (Italy)

Marco Grioni *: IPN - Ecole Polytechnique Fédérale, CH-1015 Lausanne (Switzerland).

Report:

The aim of the experiment was the investigation of the electronic structure in the series of $RNiO_3$ perovskites (R = rare earth) as a function of temperature across their metal-insulator (MI) transition. With the exception of R = Lanthanum, all nickelate compounds display MI transition, with critical temperature T_{MI} increasing with decreasing size of the rare earth ion. There is no consensus on the mechanism responsible for the instabilities [1], but recent x-ray and neutron diffraction data revealed that the MI transition is accompanied by a change of crystal symmetry from orthorombic to monoclinic. Based on the formal Ni^{3+} ($t^6_{2g}e_{1g}$) configuration, the possible ordering of the d_{x2-y2} and d_{z2} orbitals [2] was suggested. We have demonstrated in the case of cuprates that Resonant Inelastic X-Ray Scattering reveals final states having *d* occupation with different symmetry with respect to the ground state [3]. The *d-d* excitations are a fingerprint of the d^N configuration, and since they are dipole forbidden they can only be reached by a second-order optical process like RIXS. They appear in the spectra as a set of characteristic loss structures below the elastic peak.

The measurements were performed on ID8 using the AXES (Advanced X-Ray Emission Spectrograph, combined $\Delta E < 0.6$ eV at 850 eV) instrument installed on the beamline and operated by the group of the Politecnico of Milano. We measured resonant x-ray valence emission of the Ni $L\alpha_1$ line ($2p^63d^N$ - $2p^53d^{N+1}$ - $(2p^63d^N)$*), excited across the L_3 edge ($2p_{3/2}$, $h\nu_{IN}$ = 853 eV).

We performed a complete RIXS investigation of $PrNiO_3$ and $NdNiO_3$, at Room Temperature and below T_{MI}, i.e. at 120 K for $PrNiO_3$ (T_{MI} = 130 K) and at 160 K for $NdNiO_3$ (T_{MI} = 200 K).

Figure 1 shows emission spectra of $PrNiO_3$, at incident energies across the Ni L_3 threshold. The spectra display a weak

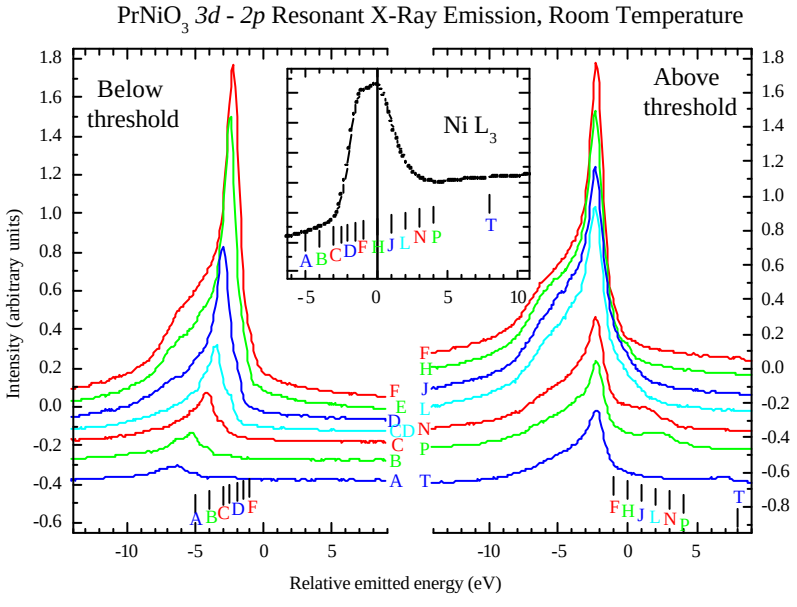

Fig. 1. *3d-2p* X-Ray Emission in $PrNiO_3$, $h\nu_{IN}$ across the L_3 edge (curve in the inset).

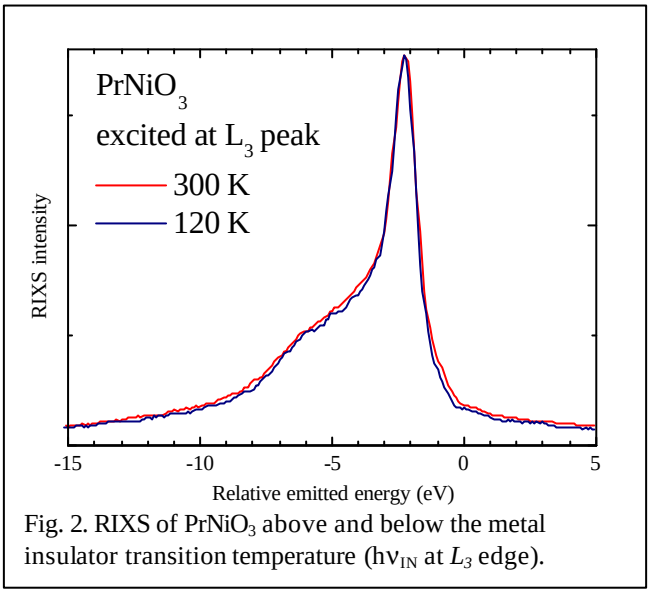

Fig. 2. RIXS of $PrNiO_3$ above and below the metal insulator transition temperature ($h\nu_{IN}$ at L_3 edge).

elastic peak and a complex lineshape arising from crystal-field and charge-transfer excitations. No differences were seen between $PrNiO_3$ and $NdNiO_3$. We also measured Oxygen *Ka* emission, which as well did not show notable changes upon rare earth subsitution.

No changes could be detected upon cooling below T_{MI} (Figure 2). By monitoring the edge jump of the absorption signal (drain current) we could see an intensity change that we attribute to the insulating behavior at low temperature. Due to their irreversibility upon heating, some observed spectral changes in RIXS during the cooling had to be attributed to contamination of the sample (a pellet of compressed powder).

The most probable reason for the lack of success of the experiment seems the heavily metallic-like, broad lineshapes that mask possible small spectral differences.

In a related proposal on ID26 (experiment HE1620) we have used high-resolution partial fluorescence yield XAS and resonant inelastic x-ray scatterin at the Ni *K* edge (*1s*, $h\nu_{IN}$ = 8.33 keV) to observe differences in the Ni electronic structure across the MI transition in various $RNiO_3$ compounds. We could observe differences only for nickelates involving Gadolinium and Lutetium, i.e. rare earths atoms of smaller radius that induced the strongest distortion of the lattice. The effect as observed in the Partial Fluorescence Yield spectra is shown in Fig. 3 for the case of $LuNiO_3$. A change is seen in the preedge region related to the *1s-3d* quadrupolar absorption. The effect is however very small and could be observed only for nickelates involving the late rare earths, that were not available during Experiment HE1545.

(During the mentioned experiment HE1620 we measured also cobaltite compounds, data of both families are currently under analysis and will be reported soon).

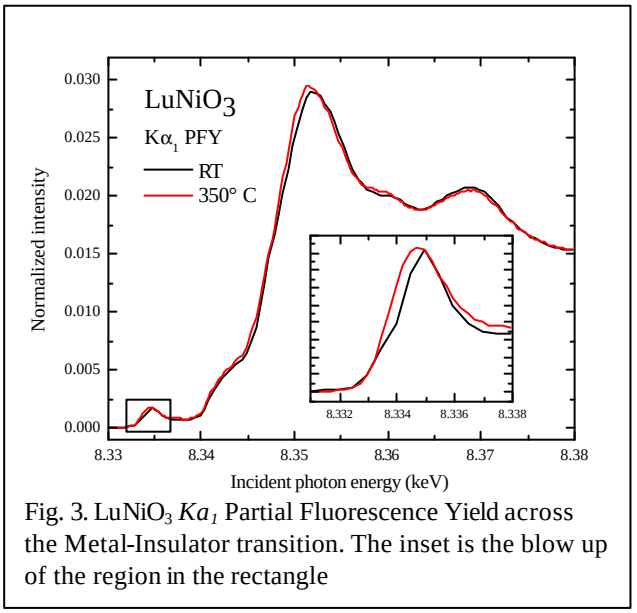

Fig. 3. $LuNiO_3$ Ka_1 Partial Fluorescence Yield across the Metal-Insulator transition. The inset is the blow up of the region in the rectangle

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[2] J.L. Garcia-Muñoz et al., Phys. Rev. B **50**, 978 (1994).
[3] G. Ghiringhelli, N.B. Brookes, E. Annese, L. Braicovich, C. Dallera, M. Grioni, L. Perfetti, A. Tagliaferri, *Phys. Rev. Lett.* 92, 117406 (2004).