ESRF	**Experiment title:** XAFS study of the local order and structure in $Y_{2-x}(Zn/Mg)_xRu_2O_7$ pyrochlores, potential new cathodes for solid-oxide fuel cells	**Experiment number**: MA-2162
Beamline: BM25A	**Date of experiment**: from: 14/03/2014 to: 19/03/2014 from: 10/09/2014 to: 13/09/2014	**Date of report**:
Shifts: 15	**Local contact(s)**: MUNOZ-NOVAL Álvaro	*Received at ESRF:*

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Report:

In proposal N.33224 we planned to perform EXAFS and XANES measurements in transmission geometry at the Ru K-edge (22117 eV) on 7 powder pellets of $Y_{2-x}(Zn/Mg)_xRu_2O_7$ pyrochlores (with x= 0.00, 0.10, 0.15, 0.20 for each Y site doping). These multifunctional oxides are potentially useful as new cathodes in solid-oxide fuel cells (SOFCs) of intermediate temperature.
In order to accurately follow the behaviour of the local order and structure parameters as a function of temperature we aimed to measure accurate spectra at 18 different temperatures between 298 K and 10 K, thickening the points in the 40 K-85 K range (being the magnetic ordering transition 55 K< T_N < 77 K, for all the compositions).
The study as a function of temperature would help us to understand the interplay between the structural, magnetic and transport properties. We wanted to check whether any short-ranged structural change is at play around the magnetic transition and how it evolves as a function of doping by Zn or Mg at the Y site.

March 2014: During the first 10 shifts we experienced serious problems in thermoregulation and temperature stabilizing due to the presence of a leak in the cryostat cold head windows. Consequently, in those days we were able to acquire spectra only between 10 and 80 K on the four $Y_{2-x}Zn_xRu_2O_7$ (with x= 0.00, 0.10, 0.15, 0.20) samples. After the cryostat change, a full

series of measurements was performed on the undoped compound in the 8 K-298 K range and on the Zn 20% doped one between 84 K and 298 K (Figure 1). No more experimental time remained to complete the planned measurements on the other two Zn-doped samples (see Figure 2) and on the four Mg-doped ones.

In Figure 1 we show that in the undoped compound a clear peak in the Debye-Waller $\sigma^2(Å^2)$ factor appears in the temperature region around the magnetic transition temperature T_N = 77 K suggesting the occurrence of a magneto-elastic coupling or of an additional local disorder. The obtained result is even more significative since in the literature neither a dynamic disorder nor a coupling between a magnetic and a structure transition were observed in these compounds previously studied by other structural techniques like diffraction. On the other hand, Raman data show an anomaly in the temperature dependence of a Raman-active mode thus assuming a spin-phonon coupling which can correspond with what we are seeing.
We hypothesize that the observed additional local disorder could be due to the presence of different Ru-O interatomic distances in the RuO_6 octahedra. The model that seems to be the most suitable is based on four shorter and two longer Ru-O distances (~2.00 Å and 2.04 Å at high temperature, respectively).
In the re-scheduling beamtime (September 2014) we have measured also the other three samples: $Y_{2-x}Zn_xRu_2O_7$ (with x= 0.10, 0.15, 0.20), in the 8 K-298 K range. The results (see Figure 2) show for x = 0.10 a remaining less intense peak in $\sigma^2(Å^2)$ just above the T_N = 55 K new transition temperature and something like a plateau for the other two compositions. Also the doped compounds σ^2 behaviour deviates from a Debye-like local order model.
We hypothesize that Zn doping, due to the lower ionic radius of Zn^{2+} respect to that of Y^{3+} and to the different oxidation state, determines an increase in the octahedra distortion and a depression of the magnetic transition also observed in a less intense magnetoelastic local effect.

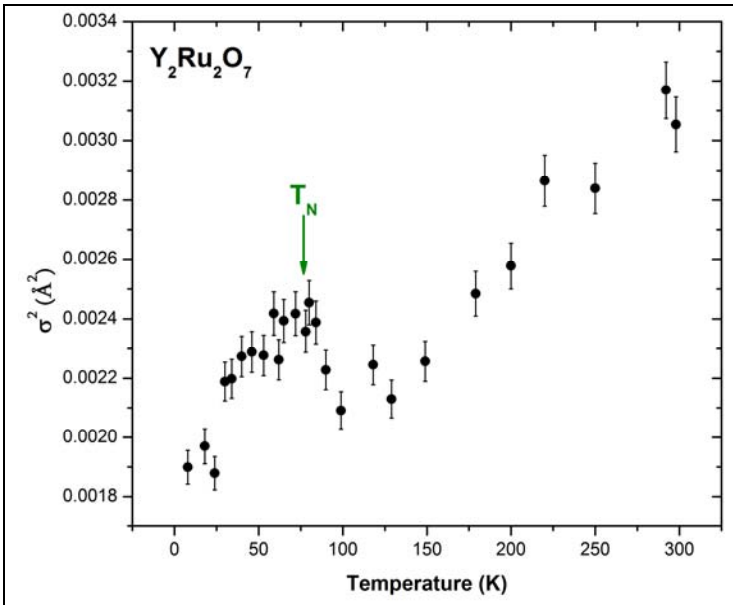

Figure 1. Ru-O mean square relative displacement $\sigma^2(Å^2)$ of $Y_2Ru_2O_7$, determined from the single shell analysis as a function of temperature (T_N = 77 K is the magnetic transition temperature for this composition).

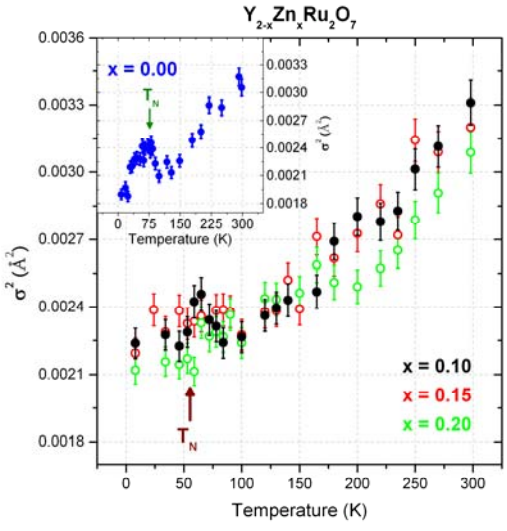

Figure 2. Ru-O mean square relative displacement $\sigma^2(Å^2)$ of $Y_{2-x}Zn_xRu_2O_7$ (with x= 0.10, 0.15, 0.20), determined from the single shell analysis as a function of temperature (inset: σ^2 for the undoped sample is reported for comparison).