



This result, coupled to the quite small value of the Debye-Waller factor for this distance, gives evidence of a direct Zr-Fe metal to metal bond [I].

- 2) Samples prepared by Combustion Synthesis according to the above method, but slowly allowed to cool down to room temperature. Iron was found to be in an oxidation state intermediate between II and III. Only the Fe-O first shell could be detected, with both Fe(II) and Fe(III) in a distorted cubic environment. The bond lengths as measured by EXAFS are 2.32(2) Å for Fe(II) and 2.018(9) Å for Fe(III).
- 3) Samples prepared by solid state reaction starting from cubic (Zr,Y)O<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>. Iron was found to be in the III oxidation state. As for the previous case, only the Fe-O first shell could be detected (bond length 1.993(6) Å), with Fe in a distorted cubic environment.
- 4) Samples prepared by solid state route as in the previous case, but then treated in flowing Ar/7%H<sub>2</sub> at 600 °C. This selectively reduces Fe in the II oxidation state, as confirmed by the XANES analysis. For these samples the same complex defect structure was found as for samples of group 1, but with only a 20% of Fe in the interstitial ½, ½, ½ position. In addition, for these samples a smaller amounts of disorder is present around the doping Fe atoms.

All the samples have been analyzed by means of X-ray powder diffraction in Pavia prior to the EXAFS measurements in Grenoble. Accordingly, all the samples have been found to be almost monophasic, the main impurity (monoclinic ZrO<sub>2</sub>) being present in amounts of c.a. 1%. For some of the samples, the XAS results have been confirmed by means of Mossbauer spectroscopy.

## References

- [1]- Paolo Ghigna, Giorgio Spinolo, Umberto Anselmi-Tamburini, Filippo Maglia, Monica Dapiaggi Gabriele Spina, Luciano Cianchi, *J Am. Chem. Soc.*, submitted.
- [2] - Paolo Ghigna, Giorgio Spinolo, Umberto Anselmi-Tamburini, Filippo Maglia, Norberto Morgante, in preparation.