XAS study of Co1-xAlx (x > 0.50) nanoparticles and structural change upon oxidation

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The main goal of this study of Co1-xAlx nanoparticles is to determine the composition and oxidation conditions which will lead to the formation of Co@Al2O3 nanoparticles, Such segregated nanoparticules should exhibit both strong magnetic moment (actually higher than bulk Cobalt) and good stability vs. exposure to air.

Small (< 3 nm) particles have actually been synthesized and structurally and magnetically characterized by Wide Angle X-ray scattering (WAXS) and SQuID (Figure 1) and indeed evidence the formation of well-defined alloys with the expected magnetic properties, especially the dramatic enhancement of the magnetic moment related to the partial oxidation of the alloy. This magnetic behaviour is in agreement with the expected segregation between a metallic cobalt core and a protective Al2O3 shell.

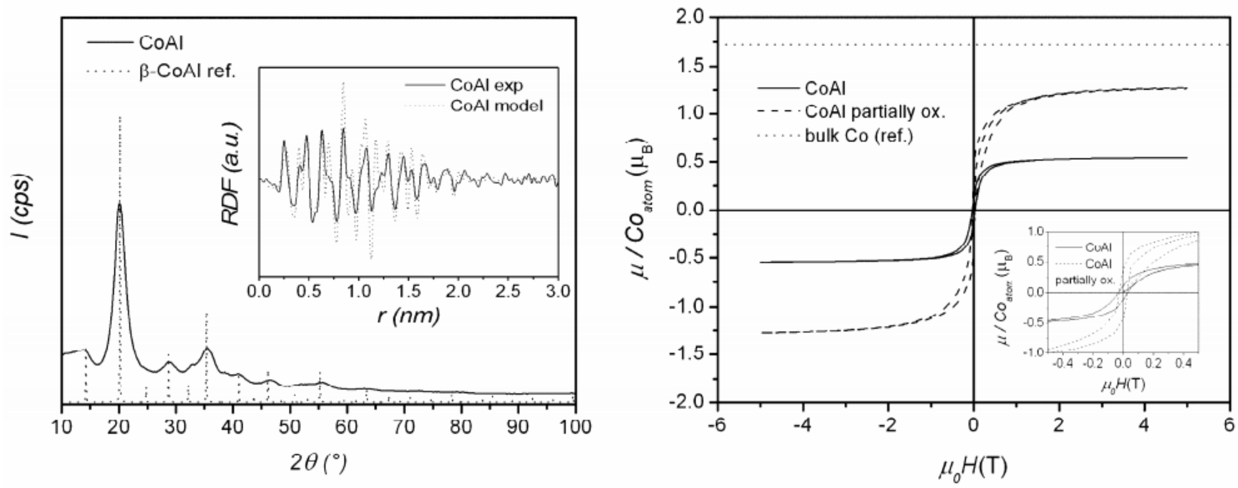

Figure1: Left, WAXS pattern of βCo1Al1 nanoparticles and the radial distribution function (shown as inset) and right, SQuID measurement at 2K on βCo1Al1 particles (solid curve) and oxidized CoAl particles (dashed curve).The hysteretic behaviour of both samples is shown in the inset.

To further investigate cobalt environment and exact oxidation state, EXAFS and XANES measurements have been performed on the E4 and C beam lines in transmission mode at room temperature on samples for different Co/Al ratios and different oxidation levels.

The shape of the XANES spectrum is different from that of hcp-Co taken as a reference. However, the position of the edge is identical (see derivative, inset Figure 2) pointing to non-oxidised Co atoms. The Fourier transform (FT) of the EXAFS data (Figure 2, right) shows a large Co–M peak overlapping the doublet expected for the ordered β-CoAl phase in good agreement with the WAXS analysis. However, XANES studies confirmed the important indication that drastic exposure to air induces cobalt oxidation. This could be related to the limited amount of Al present in the CoAl alloy, thus to the imperfect Al2O3 layer surrounding the Co core. A new two-step procedure resulted from these studies, in order to increase the thickness of the Al2O3 layer and thus improve the protection of the magnetic core. Results have been published in the European Journal of Inorganic Chemistry.

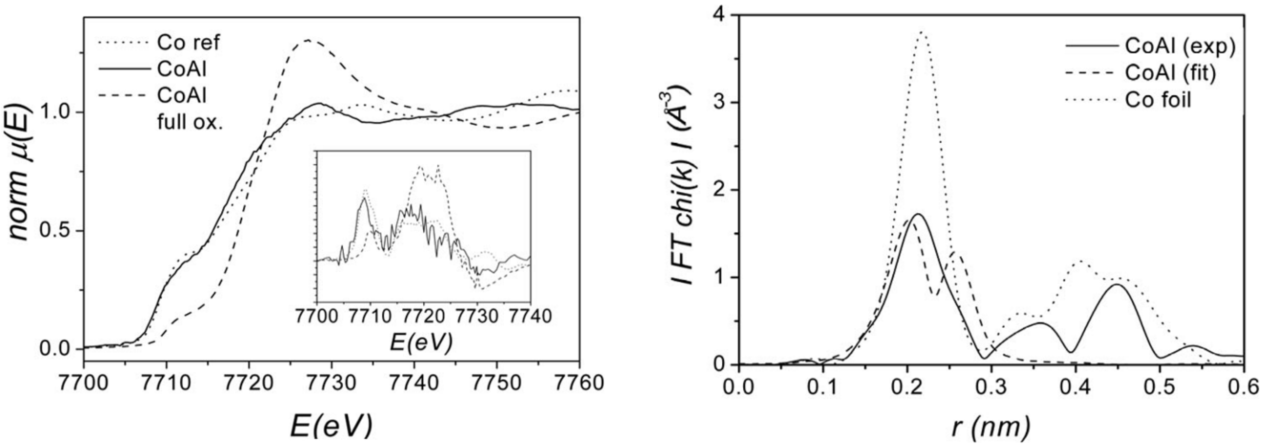

Figure 2: Normalized absorption of the Co1Al1 nanoalloy at different levels of oxidation and related Fourier Transforms.

References

[1] M. Cokoja, H. Parala, A. Birkner, R. A. Fischer, O. Margeat, D. Ciuculescu, C. Amiens, B. Chaudret, A. Falqui, and P. Lecante, Eur. J. Inorg. Chem. (2010), DOI: 10.1002/ejic.200901228.