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| ESRF | **Experiment title:**<br>Structure and Bonding of metal nanowires and clusters using EXAFS and XANES | **Experiment number**:<br>CH-1076 |
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**Introduction**

Our EU-funded research network CLUPOS, containing six European academic institutions in four countries, studies metal clusters and nanowires on surfaces and in confinements with regular spacings, and evaluates their future applications in nano-electronics and catalysis [1]. The metal clusters span the size range 1nm to 50nm in diameter, at the borderline between molecular and colloid chemistry. [2]. Metal nanowires grown within mesoporous alumina membranes are of special interest. The pore diameters are monodisperse and controllable within the 5 – 100 nm range. The pores can be filled electrochemically with different metals to give a new type of supported and insulated one-dimensional "quantum wire" [3].

Essential objectives are to use EXAFS to characterise the geometrical structures and interatomic distances of the metal clusters and nanowires, and to use XANES to give insight into their electronic structures [4]. Our experiments were carried out on three different types of sample: copper/copper oxide/cerium nanoparticles (L. R. Wallenberg, Lund); bimetallic colloids (B. Chaudret, Toulouse); and metal nanowires (G. Schmid, Essen).

**Experimental**

The wide energy range of BM29 with a Si 311 monochromator permitted all our studies to be carried out in a single run. However it led to low S/N ratios for the Co K-edge data, near the low-energy limit. Cu clusters were studied as 13mm pellets containing appropriate amounts of sample pressed with boron nitride; data were collected at 20 K in fluorescence mode to avoid problems caused by the high X-ray absorption of the Ce $L_3$ edge. Bimetallic colloids, which are air-sensitive, were studied as powders in sealed capillary tubes; data were collected in fluorescence at ambient temperature. Metal nanowires were studied as solid alumina membranes; data were collected in fluorescence mode at 20K.

**Results and discussion**

Initial results from these recent experiments are reported here; analysis of other datasets is still in progress.

*Copper clusters* (L. R. Wallenberg, Lund): Catalysts based on copper/copper oxide/cerium nanoparticles of 5–15 nm diameter, produced by inert gas condensation (IGC), had been partly characterised by HREM and XPS [5]. The highest catalytic activity is obtained with 10%–20% Cu. Despite relatively poor signal/noise ratio we successfully collected data at Cu K-edge for 6 different samples of different copper content. Data

refinement confirms the amorphous character of the copper phase which is mainly present as oxide with a four fold coordinated copper. Slight variation of the oxidation state as a function of the chemical treatment was also found. These results combined with those of our high-energy diffraction study [6] will permit all the oxide phases present this system to be characterised. This is essential for understanding and controlling the catalytic activity.

*Bimetallic platinum clusters* (B. Chaudret, Toulouse): Bimetallic clusters with applications as catalysts are prepared by co-decomposition of organometallic precursors. These clusters are monodisperse, in the size range 150 – 500 atoms [7]. We studied three bimetallic cluster systems shown by high-resolution electron microscopy to undergo major structural changes as a function of composition. These were Co-Rh clusters, Co-Pt clusters and Ru–Pt clusters. Co K-edge, Ru K-edge and Pt $L_3$-edge XAFS data were collected to study these structural changes, and to determine (from coordination number patterns) whether the metals in these bimetallic particles are alloyed or segregated into core-shell structures. Data analysis is still in progress. However, it is clear from the Co K-edge XANES that the cobalt in these clusters was partially oxidised. It will be necessary to collect further Co K-edge data on fresh samples to complete this study.

*Metal Nanowires in mesoporous alumina membranes* (G. Schmid, Essen):. **Fe nanowires** in $Al_2O_3$ covering a wide range of pore sizes (5 – 100 nm) were studied by Fe K-edge XANES and EXAFS. The nanowires were found to adopt the same bcc structure as their bulk form. On the other hand their XANES spectra show the suppression of a resonance peak close to the edge as compared with their bulk form. The XANES of the different samples investigated is presented in **Fig. 1**. These nanowires have unusual magnetic properties (susceptibility, Mössbauer) [8]. The dependence of their electronic structure on diameter, shown by XANES, is the key to understanding this behaviour.

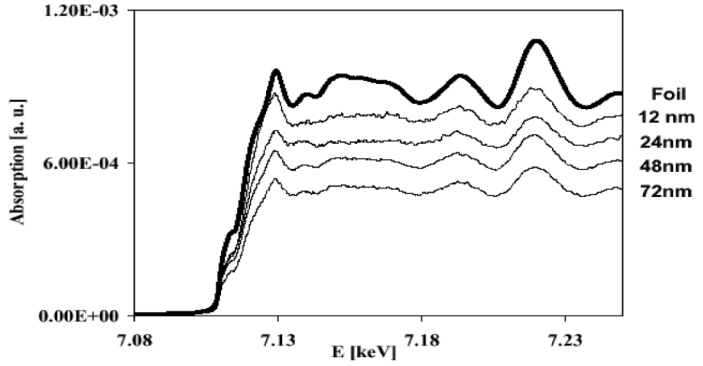


**Fig. 1:** Fe K-edge XANES for iron nanowires within alumina membranes with pores of different diameters. XANES of bulk iron is shown for comparison.

Our high-energy diffraction measurements of **Co nanowires** in $Al_2O_3$ [6,9] have shown that they have mixed hcp/fcc structures. There is a strong c-axis orientation within the $Al_2O_3$ pores. In bulk cobalt, the fcc phase is normally stable only at high temperatures. Co nanowires were studied by Co K-edge XANES and EXAFS. The data unfortunately suffered from a low signal/noise ratio and numerous glitches. Further EXAFS studies will be necessary to complete the full structural characterisation which is essential to understand the magnetic properties [8] of these materials.

**Sn nanowires,** which are diamagnetic and potentially superconducting, were studied at the Sn K-edge. The EXAFS data refinement shows that the tin has a tetragonal β-structure. There is no evidence for the cubic α-phase normally found at low temperatures.

## References


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