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Report:

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]. Structural characterisation of these metal clusters and nanowires is essential to understand their physical properties.

The objective of this experiment was to finish two cobalt K-edge EXAFS studies which we had been unable to complete during experiment CH-1076 (BM29, June 2001) [3]. These were of bimetallic Co-Rh and Co-Pt clusters (B. Chaudret, Toulouse) and Co nanowires in mesoporous alumina (G. Schmid, Essen). New data were succesfully collected from samples of both these systems. In addition, we collected a cobalt K-edge dataset from a sample of a new type of nanowire: CoI_2 contained in single-walled carbon nanotubes.

Bimetallic clusters (B. Chaudret, Toulouse): Bimetallic clusters, monodisperse in the size range 150 – 500 atoms, and with applications as catalysts and magnetic materials, are prepared by co-decomposition of organometallic precursors and stabilised by polymers such as poly(vinylpyrrolidone) [4, 5, 6]. In experiment CH-1076 we collected Co K-edge data from bimetallic Co-Rh and Co-Pt colloids, but the XANES showed that the cobalt in these clusters was partially oxidised, despite the protective polymer matrix [3].

For our new experiment, bimetallic colloids were prepared on a higher-quality vacuum line and sealed as powders in thin-walled Lindemann glass capillary tubes to prevent oxidation. Data from these samples were collected in fluorescence mode at ambient temperature. We also examined samples in the form of pellets, pressed in a glove box and sealed under an oxidation-protective layer. These compact pellets are more highly concentrated, allowing data collection in transmission mode, and can be reliably mounted in a cryostat at low temperatures. The cobalt K-edge XANES confirmed that both types of protected sample are resistant to oxidation. Co K-edge EXAFS data were obtained from colloids with different metal composition ratios. These are currently being refined to determine the interatomic distances, geometric structures, and the coordination number patterns around the cobalt atoms, which will distinguish whether the metals in these bimetallic particles are alloyed or segregated into core-shell structures. We plan to study a further range of the Co_xRh_{1-x} materials by Rh K-edge EXAFS to complete the structural characterisation of this system.

Metal nanowires in mesoporous alumina membranes (G. Schmid, Essen): Cobalt nanowires in mesoporous alumina membranes have unusual magnetic properties [7]. Our high-energy diffraction measurements of the Co nanowires have shown that they have mixed hcp/fcc structures [8, 9]. 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. Our previous Co K-edge EXAFS study of these nanowires used the Si(311) monochromator, for which the Co K-edge was at the low end of the accessible energy range, giving data with a low signal/noise ratio and containing glitches [3]. The new experiment used the Si(111) monochromator. We repeated the measurements on the previous samples, together with some freshly prepared samples with pore diameters 12nm, 24nm, 48nm and 72nm. We successfully obtained EXAFS data of better quality, with cobalt foil in the monitor position, which will allow a full structural refinement to complement the diffraction studies.

CoI_2 nanowires in single-walled carbon nanotubes: Single walled carbon nanotubes (SWNTs) are emerging as ideal model systems for studying atomically regulated crystal growth [10]. Open SWNTs, terminated at one end by fullerenic carbon hemispheres, form well-defined cylindrical cavities with a strictly limited diameter range (typically 1–2 nm). The internal van der Waals surfaces of SWNTs regulate the growth of encapsulated materials very precisely. Nanoscale crystals with integral layer architectures and reduced coordination structures can be formed. Dr J. Sloan (Oxford) has established a method of filling open SWNTs with metal halide nanowires, introducing molten halide salts into the SWNTs by capillary wetting at high temperature under vacuum [11]. These new materials have been characterised principally by high-resolution transmission electron microscopy, which gives local structural information on individual nanowires. In a new collaboration with Dr. Sloan, we tested the possibility of characterising them more fully using EXAFS.

We studied a sample of CoI_2 nanowires in SWNTs pressed into a 13mm pellet with boron nitride. Co K-edge data were collected in fluorescence mode because of the low metal concentration, and to avoid problems caused by the high X-ray absorption of the iodine L_3-edge. The sample temperature was 80K. EXAFS data were successfully collected with high S/N ratio to k = 12 $Å^{-1}$ from a single 1-hour scan. Preliminary analysis shows a Co–I nearest neighbour distance expanded from the bulk CoI_2 used as a reference, with a reduced coordination number of the cobalt atoms.

This is the first EXAFS experiment on a metal halide nanowire in a SWNT. It confirms the feasibility of EXAFS structural characterisation of these new materials. We plan to develop this in a future study.

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