



**Experiment title:** Structural anisotropy of metal nanowires confined in nanoporous alumina membrane using high energy diffraction

**Experiment number:**  
HS-1439

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### Introduction

There is a remarkable trend in materials research to prepare and characterise nano-materials of quantum-dot size in regular arrangements [1]. For instance, self-assembly of magnetic transition metals (Fe, Co and Ni) nano-particles have recently attracted attention for their potential use as new storage devices [2]. A promising way to achieve a regular array of nanomaterials is to use mesoporous alumina membranes as a template to grow metal nanowires in confinements with regular spacings. In the framework of our EU-funded research network CLUPOS [3] we have prepared a series of, Fe, Co, Sn, Ni nanowires adsorbed into mesoporous alumina membranes of pore size varying from ca. 5 to 72 nm. These represent isolated one-dimensional quantum wires with prospective applications in electronic devices [4]. The physical properties of these nano-materials are expected to be different from the bulk form. For instance the ferromagnetic samples (Fe and Co) feature unusual magnetic properties [5]. To achieve a better understanding of the physical properties of these new nanomaterials, and the influence on them of the support material, we carried out a structural characterisation using High Energy Diffraction, focusing on their anisotropic properties. These measurements complement our EXAFS studies of metal nanowires [6-8].

### Results and discussion

The very high quality of diffraction patterns taken with the image plate detector on ID15B demonstrates the remarkable capability of this equipment in terms of characterisation of preferred orientation. Our results are exceptional considering the very low metal content of the samples (<1% by weight). HED is capable of giving much more valuable information on the anisotropy of the structure than ordinary diffraction methods such as WAXS. The membranes were mounted on a special sample holder allowing a full rotation ( $\phi$ -variation) of the samples on 360°, and investigated face-on and edge-on to the incident beam.

### **Iron nanowires**

Fe nanowires grown in 10, 20, 40 and 60V membranes were investigated [7]. Iron nanowires were found structurally similar to bcc bulk iron. They present no sign of oxidation. **Fig. 1** shows the high energy diffraction pattern of the 24 nm pore diameter. A strong preferred orientation with the [111] or [110] directions perpendicular to the pore axis can clearly be seen on this pattern. The ratio of the two preferred orientations is also sensitive to the pore diameter. Fe nanowires in Al<sub>2</sub>O<sub>3</sub> have been found from susceptibility measurements and Mössbauer spectroscopy to have unusual magnetic properties that depend on the pore size [5]. The preferred orientation could be an explanation of their unusual anisotropic magnetic properties.

## Cobalt nanowires

Cobalt nanowires grown in 10, 15, 20, 40 and 60V membranes were investigated. The measurements show that Co nanowires are composed of a mixture of two different phases: the hcp phase, stable at room temperature, and the fcc high temperature  $\beta$ -form of Co, that is normally only stable above 417°C. The ratio depends on the pore size [7]. The high energy diffraction pattern of the 48 nm pore diameter is shown in **Fig. 2**. The Co nanowires present a very strong preferred orientation with the [100] direction perpendicular to the pore axis for both fcc and hcp structures [7]. This effect seems to be very sensitive to the pore diameter. However the relationship between pore size and ratio of the two preferred orientation (phase) is not linear. The proportion of the two phases is also sensitive to the voltage of Co nanowire deposition. Magnetic measurements also showed very different results according to the pore size [5]. This could be explained by the different ratio of phase and/or preferred orientation found by these diffraction measurements. The complexity of this system demands further investigations in that direction.

## Tin and Nickel nanowires

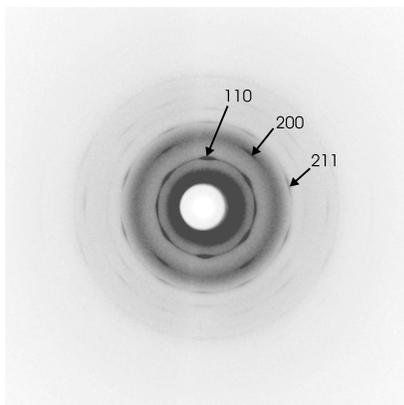
Tin nanowires grown in 10, 20, 40 and 60V membranes were investigated. Tin nanowires adopt the tetragonal structure and feature a very strong preferred orientation with the [100] direction perpendicular to the pore axis. Nickel nanowires grown in 10 and 20V membranes adopt the same fcc structure as bulk nickel but no sign of preferred orientation could be seen in the HED pattern.

## Bimetallic copper/cerium nanoclusters

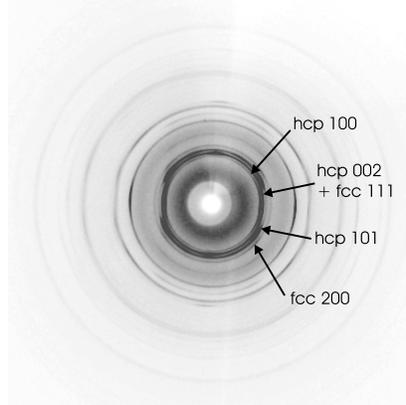
Additionally, we studied a series of copper/copper oxide/cerium nanoparticles which have high catalytic activity [9]. This complements our EXAFS study of this system [8]. All the oxide phases present in samples of different copper content and preparation method were characterised.

## Conclusions

Except for the cobalt, the nanowires adopt the same structure as their bulk form. For the cobalt, a mixture of fcc and hcp phases was observed in a ratio depending on the pore sizes. The metal nanowires are polycrystalline and composed of crystallites showing a great variation of orientation according to the metal type and the pore size. The sensitivity of the phase type or/and the preferred orientation of Co and Fe as a function of the pore size is the key to understanding their magnetic behaviour. The confinement of these metal nanowires in the alumina membrane pores seems to confer them very unusual structure and properties.



**Fig. 1:** (left) 2D diffraction pattern of a 20V alumina membrane filled with Fe nanowires [7]



**Fig. 2:** (right) 2D diffraction pattern of a 40V alumina membrane filled with Co nanowires [7]

## References

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