ESRF	**Experiment title:** SAXS Structural Investigation of Organised Nanomaterials: Mesoporous Alumina Membranes, and Membranes containing Metal/Semiconductor Nanowires	**Experiment number**: ME-348
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The controlled organisation of nano-materials in arrays of confinements with regular spacings is a key issue in fabricating functional nanodevices. Structural characterisation of these materials is essential for understanding their physical properties and evaluating their future applications in nano-electronics.

Metal nanowires grown within mesoporous alumina membranes are of special interest. These membranes, made by an electrochemical anodic process, contain ordered hexagonal arrays of parallel pore channels, perpendicular to the surface [1]. The pore diameters are monodisperse and controllable within the 5–250 nm range, with wall thickness comparable to pore diameter. The pores are filled electrochemically with metals to fabricate a new type of supported and insulated one-dimensional "quantum wire" [1]. These have unusual properties. For instance Fe, Co and Ni nanowires in Al_2O_3 have magnetic properties (susceptibility, Mössbauer) that vary with pore diameter [2].

Our experiment was in four main parts: SAXS studies of mesoporous alumina membranes, SAXS studies of membranes containing cobalt nanowires, SAXS studies of membranes containing gallium nitride nanowires, and anomalous SAXS (ASAXS) studies of membranes containing cobalt nanowires. Additionally, we made SAXS measurements of self-assembled metal nanoparticles in an organic matrix. The 2D patterns were radially integrated using the ESRF software package FIT2D to display the intensity profile as a function of the scattering angle or vector.

SAXS of mesoporous alumina membranes: We previously studied alumina membranes with pore sizes between 5 nm and 72 nm using SAXS on beamline ID01 [3]. This work showed that SAXS represents a powerful method of characterising the structures of these partially ordered mesoscopic materials on several different length scales, including pore separation and long-range regularity. In experiment ME-348 we extended these studies to higher *k*-values, to cover the Porod intensity region. We also made measurements on membranes with larger pore sizes, up to 170 nm. The SAXS intensity profiles, which cover several orders of magnitude, show Bragg peaks arising from the structure factor for the two-dimensional arrays of parallel pore channels. These patterns show variations in the azimuthal intensity as the membranes are rotated in the beam, changing systematically in a complex sequence from a ring structure for the face-on position with pores parallel to the X-ray beam to a set of vertical spots for the edge-on position. Analysis and modelling of the data is in progress in an attempt to separate the cylindrical form factor for the pore volume from the structure factor. If this can be achieved it will represent a direct measurement of pore diameters.

Additionally, we studied the effect of pore length on the SAXS by using membranes of different thickness and in stacked layers. The SAXS profiles were attenuated as membrane thickness increases. This suggests that absorption effects, which are usually neglected in the SAXS formalism, may be important for this porous membrane system.

SAXS of membranes containing cobalt nanowires: Cobalt nanowires have electron density almost exactly double that of the alumina host, and on the basis of their X-ray scattering contrast would be expected to give an intensity profile the same shape as that of the empty membrane. However an initial measurement [3] using membranes with 48 nm pore diameter showed a more substantial modification of the pattern. In experiment ME-348 we studied alumina membranes with pore diameters between 12 nm and 170 nm. Matched samples were prepared for each pore size; one

membrane of each pair was filled with cobalt. In the Co-filled membranes, the peaks were slightly displaced, and the oscillatory amplitude was reduced [Figure 1]. This increased disorder in the SAXS profiles suggests that the distribution of Co does not correspond precisely to the void volume of the empty pores. Some nanowires may be discontinuous, or there may be some empty pores, converting the assembly to a three-phase system. Further data analysis is in progress.

SAXS of membranes containing gallium nitride nanowires: GaN has electron density almost exactly equal to that of alumina, and so is an almost exact contrast match with the Al_2O_3 host. The SAXS pattern will therefore permit the degree and regularity of pore filling to be measured. Data were successfully obtained and analysis is in progress.

ASAXS of membranes containing cobalt nanowires: In this part of the experiment the cobalt nanowires were studied by anomalous SAXS, using X-ray energies below and above the Co K absorption edge. The aim was to see if the contribution of the cobalt atoms to the SAXS pattern could be separated, allowing the extent of pore filling to be evaluated, which is necessary for a quantitative interpretation of the ferromagnetic properties. Preliminary analysis of the results shows that, as well as the obvious decrease in scattering intensity as the X-ray energy is increased across the absorption edge, there are subtle changes to the shapes of the peaks in the scattering profiles.

SAXS studies of metal nanoparticles: Co and NiFe nanoparticles (2.7 to 3.3 nm diameter) of narrow size distribution have been obtained by decomposing organometallic precursors in organic solutions of long alkyl chain ligands. WAXS has shown that both adopt the bulk structure: HCP in the case of cobalt; a mixture of FCC and BCC for NiFe. In this experiment we used SAXS to complement electron microscopy studies of the self-assembly of these nano particles upon solvent evaporation. In *k*-space, a sharp peak was observed for each sample at values corresponding to distances of about 5 nm, which we attribute to interparticle distances [Figure 2]. The absence of peaks at lower *k*-values evidences the absence of long range order in the solids.

Results from these experiments, and our data analysis so far, have now been been presented at international conferences and published. The results from CH-810 and ME-348 on SAXS of alumina membranes and Co nanowires were presented at the 6th International School and Symposium on Synchrotron radiation in Natural Science, Jaszowiec, Poland, 2002 [4]. The results from ME-348 on SAXS and ASAXS of Co nanowires, and SAXS of the metal nanoparticles, were presented the Faraday Discussion 125 "Nanoparticle Assemblies", Liverpool, July 2003 [5, 6].

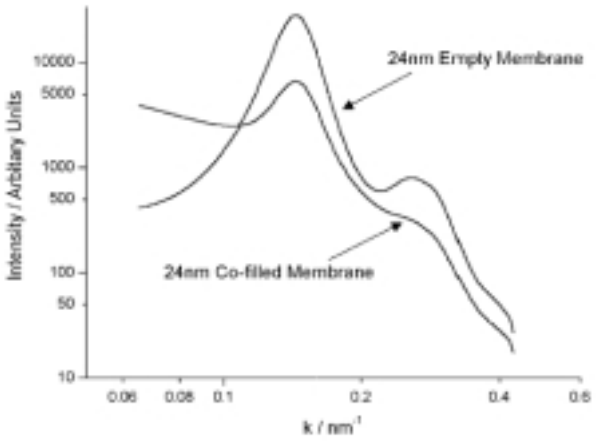

Fig. 1 SAXS intensity profile from a cobalt-filled AAO membrane, compared with that from a matched empty membrane. [5]

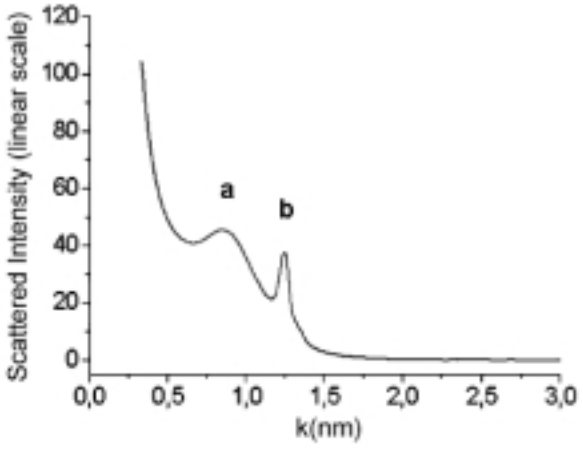

Fig. 2 SAXS of self-assembled NiFe nanoparticles [6]

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