Structure of assemblies of metal nanowires in mesoporous alumina membranes studied by EXAFS, XANES, X-ray diffraction and SAXS

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Mesoporous alumina membranes (“anodic aluminium oxide”, or “AAO”) are made by anodic oxidation of aluminium metal. These membranes contain hexagonal arrays of parallel non-intersecting cylindrical pores perpendicular to the membrane surface. By varying the anodisation voltage, the pore diameters are controllable within the range 5–250 nm. We have used AAO membranes as templates for the electrochemical deposition of metals within the pores to produce nanowires. These represent assemblies of one-dimensional quantum wires with prospective applications in electronic, optoelectronic and magnetic devices. Detailed characterisation of the structures of these nanowire assemblies on a variety of length scales is essential to understand their physical properties and evaluate their possible applications. We have used EXAFS, XANES, WAXS, high energy X-ray diffraction and SAXS to study their structure and bonding. In this paper we report the results of our studies of four different nanowire systems supported in AAO membranes. These are the ferromagnetic metals iron and cobalt, the superconducting metal tin, and the semiconductor gallium nitride. Iron nanowires in pores of diameter over the range 12 nm–72 nm are structurally very similar to bcc bulk iron. They have a strong preferred orientation within the alumina pores. Their XANES shows significant differences from that of bulk iron, showing that the electronic structure of the iron nanowires depends systematically on their diameter. Cobalt nanowires are composed of a mixture of hcp and fcc phases, but the ratio of the two phases does not depend in a simple way on the pore diameter or preparation conditions. In bulk cobalt, the fcc β -phase is normally stable only at high temperatures. Strong preferred orientation of the *c*-axis in the pores was found. Tin nanowires in alumina membranes with pores diameters between 12 nm and 72 nm have a tetragonal β -structure at ambient temperature and also at 80 K. Magnetic susceptibility

measurements show that they are diamagnetic, and become superconducting at the same temperature as bulk tin (3.7 K). Gallium nitride nanowires have been prepared in alumina membranes with pore diameter 24 nm by a novel method. Gallium nitrate was deposited in the pores from aqueous solution and thermolysed at 1000 °C to form Ga₂O₃, which was reacted with ammonia at 1000 °C. The GaN nanowires have the wurtzite structure. Preparation at 1150 °C led to the incorporation of aluminium in the GaN. The mesoscopic ordering of the pores in the AAO membranes and their filling by metal nanowires has been studied by SAXS, which shows patterns of Bragg peaks arising from the pore arrays. Additionally, the cobalt nanowires have been the subject of an initial ASAXS study.

Introduction

Mesoporous alumina membranes (“anodic aluminium oxide”, or “AAO”; sometimes called “alumite”) are produced by anodic oxidation of aluminium metal in a polyprotic acid, following a process known for fifty years.^{1,2,3} The membranes, composed of alumina which is amorphous to X-ray diffraction, have pore diameters in the range 5–250 nm, with pore densities up to 10¹¹ cm⁻². The pores are cylindrical, and form regular hexagonal arrays of parallel non-intersecting channels perpendicular to the membrane surface. The pore diameter increases linearly with anodisation voltage, while the anodising time determines the membrane thickness up to several hundred µm.

These AAO membranes have been manufactured for many years for use in filtration processes, although commercial availability⁴ is restricted to pore diameters of 20 nm, 100 nm and 200 nm. They are now finding possible uses in a new range of scientific applications, and have attracted substantial interest as host or template structures.

There have been many reports of the production within the pores of AAO membranes of assemblies of metal clusters and colloids,^{5,6} metal nanowires,^{7–16} semiconductor nanowires^{8,10,11,16–18} and other systems such as electrically conducting polymers,^{8,11} luminescent siloxenes,^{12,16} luminescent organic compounds¹⁹ and carbon nanotubes.^{20,21} The structural regularity of the pore arrangements in AAO membranes gives them a huge advantage as templates for nanowire assemblies over other types of porous membrane, such as track-etched polycarbonates,^{8,11,22} in which the individual pores are also of uniform size, but their arrangement in the membrane is random.

Assemblies of metal nanowires within the mesoporous alumina membranes are of special interest because they can be regarded as a new type of assembly of supported and insulated one-dimensional “quantum wires”. Prospective applications include nanoscale magnetic, electronic, and optoelectronic devices. Electrochemical deposition is the method of choice for the production of metal nanowires in the AAO membranes, although other methods such as injection of molten metal⁹ and thermal decomposition of metal salts²³ have also been used.

Nanowires of many different metals have been prepared within AAO membranes. There have been two major focusses of these studies to date: optical and magnetic properties.

Small particles of many metals have well-resolved absorption bands in the visible region.²⁴ The optical properties of nanowires of metals such as gold^{11,16,25,26} and platinum²⁷ are very sensitive to diameter and aspect ratio. For this type of study it is significant that the AAO membranes themselves are optically transparent.

Nanowires of ferromagnetic metals (iron, cobalt and nickel) have obvious prospective applications in magnetic recording and memories.²⁸ Here, not only the size control of individual nanowires is important, but also the imposition by the alumina template of a mesostructure of regularly-spaced parallel wires. It has been estimated that a bit density several times greater than that currently possible could be achieved from this type of composite material.²⁹ The nanowire diameters can be smaller than the magnetic domain size in the bulk metals, causing unusual magnetic properties. Additionally, any structural anisotropy or preferred orientation of the metal lattice in the pores will be important in controlling the magnetic axis direction, especially for metals with hexagonal lattices.

Bimetallic layered nanorods, such as gold-platinum,³⁰ have also been synthesised in mesoporous alumina, by electrochemical deposition from a sequence of different solutions. In this example, the

alumina membrane was subsequently dissolved completely, to produce free nanowires in solution, which could then be derivatised and processed for a variety of applications. It was reported that this type of multi-layered nanowire could form the basis of giant magnetoresistance sensors.³⁰

There is wide scope for studies of nanowires of other metals possessing different properties such as antiferromagnetism or superconductivity, which might be modified by the size restriction imposed by the AAO template. Additionally, alloy nanowires can be prepared by co-deposition.³¹

AAO membranes have also been used to host assemblies of nanowires of semiconductors such as cadmium sulfide,^{10,16,17} gallium arsenide¹⁰ and gallium nitride.^{16,18} The nanowire diameters can be smaller than the excitons in the bulk semiconductors, modifying the semiconductivity properties in a controlled way.

Despite intense interest in the preparation and properties of metal and semiconductor nanowires within mesoporous alumina membranes, structural characterisation of most of these exciting new materials is inadequate for a full understanding of their properties and potential applications. In many cases, structural characterisation has been limited to determination of the lattice type and parameter by simple one-dimensional X-ray diffraction. Electron microscopy and atomic force microscopy have been widely used to achieve direct imaging of the nanowires in their host material, but these methods cover only local areas of sample which may not be representative of the whole nanowire assemblies.

Comprehensive structural characterisation of these novel AAO-supported nanowire materials is an essential prerequisite to understanding and controlling their physical properties. Our strategy has been to carry out a detailed structural study of metal nanowires within mesoporous alumina using a variety of methods, each based on the use of synchrotron radiation X-rays. We have used extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) spectroscopy, wide-angle X-ray scattering (WAXS), high-energy X-ray diffraction (HED) and small-angle X-ray scattering (SAXS and ASAXS). This powerful combination of complementary methods has achieved the characterisation of lattice types, interatomic distances, disorder factors, crystallite sizes, preferred lattice orientations and long-range structural ordering of the nanowires within the alumina pores.

We previously used EXAFS to show that gold nanowires have the same lattice structure and almost identical interatomic distances as bulk gold. Their very low EXAFS Debye–Waller factors were interpreted as indicating a high crystallinity, implying that the nanowires have a very small degree of structural disorder.¹⁴ XANES showed clearly the progressive development of metallic electronic structure with increasing nuclearity in a series of gold clusters, colloids and nanowires.¹⁴ We have also reported initial structural results on nanowires of silver, copper, iron and cobalt in a limited range of AAO pore sizes.¹⁵ Additionally, the mesoscopic ordering of the pores in the AAO membranes themselves, and their filling by cobalt, has been studied using SAXS, which shows patterns of Bragg peaks arising from the pore arrays.^{32,33}

In this paper we report the results of our studies of four different nanowire/AAO systems: the ferromagnetic metals iron and cobalt, the superconducting metal tin, and the semiconductor gallium nitride.

Methodology

Our strategy has been to apply a powerful combination of complementary methods, each based on the use of synchrotron radiation X-rays, to study the structures of nanowires within mesoporous alumina membranes on a variety of length scales.

Extended X-ray absorption fine structure (EXAFS) is widely used for structural characterisation of materials lacking long-range crystalline order.³⁴ EXAFS is a whole-sample method which gives the local atomic structure of the metal nanowires around the absorbing atom, specifically the nearest neighbour interatomic distances and coordination numbers, up to about the fourth nearest neighbours. Small structural differences between the nanowires and the corresponding bulk metals can therefore be studied. The Debye–Waller factors give information on structural disorder, with analysis of spectra taken at different temperatures permitting separation of static and dynamic disorder. Account can also be taken in the data analysis of any asymmetry in the bond length distribution, giving important insight into the vibrational behaviour of the nanowires. Because of the use of monochromatic radiation, EXAFS is element-selective, and consequently well suited to

samples containing more than one type of metal atom. Additionally, it is not necessary to remove the aluminium backing from the AAO samples to study them by EXAFS.

The X-ray absorption spectrum used for the EXAFS analysis also contains important information in the region near the absorption threshold of the absorbing atom. This technique of X-ray absorption near-edge structure spectroscopy (XANES) can characterise the chemical bonding environment of the absorbing atom, and can give a measure of the real oxidation state of the metal atoms in the nanowires.³⁵ This allows any chemical oxidation of the nanowires to be detected and also permits study of possible electron density transfer between the nanowires and their supports. The data are collected with simultaneous monitoring of a metal foil as reference, permitting exact calibration of X-ray energies and reliable detection of any small XANES differences between nanowires and bulk.

Wide-angle X-ray scattering (WAXS) resembles conventional X-ray diffraction, studying the well-defined Bragg peaks from a crystalline material to give the overall lattice structure and an independent measurement of metal-metal distances extending to much longer range than EXAFS. The AAO host membranes are X-ray amorphous, so metal nanowires within their pores can be studied by this method. Additionally, the width of the diffraction peaks directly gives the size of the individual crystallites in the polycrystalline nanowires through the Scherrer equation. However, WAXS is not element-specific.

A major limitation of one-dimensional X-ray diffraction is that it cannot reveal any structural anisotropy in the nanowires. Two-dimensional diffraction patterns are the key to this problem. High-energy diffraction (HED) uses X-rays of much shorter wavelength, causing the principal diffraction angles to be compressed within a solid angle of a few degrees around the path of the incident beam. This permits the entire diffraction pattern to be recorded as a two-dimensional image on a detector plate of reasonable size. Consequently, as well as giving information on the lattice type and spacings, and particle sizes, which is also obtainable from WAXS or conventional one-dimensional diffraction, HED allows study of structural anisotropy. In the present context, this refers to preferred orientations of the nanowire lattices within the AAO pores. For WAXS and HED experiments, it is necessary to remove the aluminium backing from the AAO membranes, because otherwise the Al lattice dominates the diffraction pattern.

Small-angle X-ray scattering (SAXS) makes use of the coherent scattering and interference effects arising from variations in the electron density of a composite sample.³⁶ The observed SAXS intensity profile derives from the spatial heterogeneity of the sample material and is therefore sensitive to the size, shape and orientation of pore volume. Although SAXS, together with the related method of small-angle neutron scattering (SANS), has been extensively used for the study of porous solids, there is surprisingly little previous work on its application to membranes containing regular arrays of parallel pores. SAXS has the potential to characterise the structures of these membranes on several different length scales: pore diameter, pore separation, pore length and aspect ratio, pore continuity and variation of pore diameter along the length.^{32,33} SAXS of membranes containing nanowires can show the extent to which the pores are filled, because incomplete filling gives a three-phase heterogeneous system (alumina, nanowire and void). Any spontaneous organisation of the filled pores into superlattices will be shown. Additionally, the technique of anomalous small-angle X-ray scattering (ASAXS), which studies changes in SAXS intensity profiles as the X-ray energy is varied across an absorption edge of an element,^{37,38} can isolate the scattering due to fluctuations in concentration of that element contained in nanowires within the pores.

Experimental

Preparation of AAO membranes

The mesoporous alumina membranes were produced by anodising electropolished high purity aluminium foils in a polyprotic acid such as sulfuric acid or oxalic acid, using a lead plate cathode. Full details are given elsewhere.^{6,32,39,40} Pore diameters, measured by electron microscopy, are monodisperse and linearly related to the anodising voltage above 10 V (1.2 nm V^{-1}). The pores are perpendicular to the membrane surface, packed in an ordered hexagonal array with wall thickness comparable to pore diameter (Fig. 1). The membrane thickness, ranging up to several hundred microns, can be controlled by the time of the anodising process.

Fig. 1 Schematic cross section of mesoporous alumina membrane before removal of Al backing; schematic top view; atomic force microscope image for a membrane produced by anodisation at 40 V (from ref. 33, reprinted with copyright permission from Elsevier).

Pore filling with metal nanowires

Nanowires of iron,^{12,15,40} cobalt^{15,40} and tin⁴⁰ were deposited within the AAO membranes by electrochemical AC plating from an aqueous solution of the metal sulfate, with H_3BO_3 as a supporting electrolyte in the case of iron and cobalt, and H_2SO_4 in the case of tin. Full details are given in the appropriate references. For membranes with 24 nm pores, the cobalt nanowires were deposited at three different voltages: 10 V, 16 V and 20 V. Additionally, for membranes with pores 48 nm in diameter, the cobalt nanowires were grown in an external magnetic field (0.35 T) applied in directions perpendicular and parallel to the pores.

The aluminium serves as an electrode during the electroplating, and graphite is used as the counter-electrode. Because the alumina membrane acts as a rectifier, the amount of metal plated during the cathodic half-cycle is larger than the amount of metal reoxidised during the anodic half-cycle, resulting in net deposition of metal. DC plating would cause the system to become polarised. After deposition of the nanowires the aluminium can be dissolved from the back of the alumina membrane where necessary using a 10% solution of Br_2 in methanol. It is important to note that the alumina membranes which are commercially sold as filters⁴ are not supported on aluminium, and therefore cannot be filled electrochemically with metal nanowires unless a method such as sputtering is used to deposit a metal layer which can act as an electrode.

Pore filling with gallium nitride

Gallium nitride nanowires were introduced into the pores (24 nm diameter) of AAO membranes by a novel method.^{16,41} Firstly, $\text{Ga}(\text{NO}_3)_3$ was deposited into the pores from aqueous solution. After drying, the gallium nitrate was decomposed at 1000 °C to form gallium oxide, Ga_2O_3 . Because Ga_2O_3 is insoluble in water, this process can be repeated as many times as necessary to maximise filling of the pores. The Ga_2O_3 was then reacted for one hour at 1000 °C with NH_3 , diluted with a flow of nitrogen, to give crystalline nanoparticles of GaN. The formation of GaN was confirmed by ^{71}Ga NMR and powder X-ray diffraction.¹⁶ The average particle size, calculated from the half width of the X-ray diffraction peaks using the Scherrer equation, reached 23.8 nm after fivefold repeated filling with gallium oxide, corresponding almost exactly to the AAO pore diameter of 24 nm. Fifteen-, 20-, and 25-fold filling of the pores did not result in any further increase of GaN particle size.

GaN/AAO samples for our structural experiments were produced by single and five-fold filling of the pores. Additionally, in a variation of the above procedure, samples were produced by heating the gallium oxide in NH_3 at 1150 °C for 10 minutes.

Experimental measurements

EXAFS/XANES. X-ray absorption spectra were recorded on beamlines 7.1 (Si(111) monochromator, Fe and Co K-edges),⁴² and 9.2 (Si(200) monochromator, Sn K-edge)⁴³ at the SRS (Daresbury, UK); and on beamline BM29 (Si(311) monochromator, Fe, Co and Ga K-edges)⁴⁴ at the ESRF (Grenoble, France). Most samples were studied as membranes, stacked when necessary to obtain a suitable edge jump. As the Fe-containing membranes were rather brittle, some were studied without removing their aluminium backing, to protect against cracking, and a second series with the backing removed were first studied as pieces of membrane and then ground with boron nitride and pressed (5 bar) into 13 mm pellets. The GaN-containing membranes were in pieces too small to be

used directly, so were ground with boron nitride and pressed into pellets. A typical beamsize was 6 mm $\times$ 0.5 mm. The monochromators were detuned on their rocking curves to approximately half of the maximum transmitted X-ray intensity to reduce the harmonic content of the beam. Data were collected at low temperature (80 K at the SRS using a liquid nitrogen cold-finger cryostat; 30 K at the ESRF using a closed-cycled helium cryostat), operating in fluorescence mode with multi-channel solid state detectors. A typical dataset acquisition time was 1 h. Where necessary, several datasets from each sample were summed to achieve high signal/noise ratios to $k = 20 \text{ \AA}^{-1}$. Spectra of metal foils as references were recorded simultaneously in the monitor position, for accurate measurement of small shifts in the X-ray absorption energies of the nanowires.

Data reduction of the spectra was performed using the program EXBROOK.⁴⁵ Background subtraction and normalisation were carried out by fitting a linear polynomial to the pre-edge region and cubic splines to the post-edge region. EXAFS data were refined with the EXCURV98 package.⁴⁵ Phase shifts and backscattering factors were calculated *ab initio* using Hedin–Lundqvist potentials. Refinements used k^3 or k^2 weighting as appropriate to equalise the amplitudes of the weighted EXAFS oscillations over the wide range of k values covered by the data. Contributions to the higher neighbouring shells from multiple-scattering paths were calculated up to 12 Å. Possible asymmetric oscillation effects in the inter-atomic radial distributions were found to be negligible at the low temperatures of our datasets.

Crystallographic data from the CDS database⁴⁶ for the structures of bulk iron, cobalt, tin and gallium nitride were used as models for the structural refinements. The nanowire data were initially refined in different lattice structures and with independent radial shells. The high data quality made Fourier filtering unnecessary. For the presentation of the final results, the built-in programme SYMMETRY⁴⁵ was used to generate automatically all the shell parameters (co-ordination number, distance) corresponding to the appropriate lattice structure. The remaining adjustable parameters are the cell parameter, the Debye–Waller factors for every shell, E_f (contribution of the wave vector of the zero photoelectron relative to the origin of k) and the AFAC factor (amplitude reduction due to many-electron processes). This significantly reduced the number of variables in the final fitting process.

WAXS. WAXS data were collected on ESRF beamline ID01⁴⁷ operating under beam conditions of 6 GeV, 90 mA, and 16 bunch mode, using typically an X-ray energy of 8.227 keV, corresponding to a wavelength of 1.5070 Å. The alumina membranes filled with electrochemically grown metal nanowires were mounted as films in the X-ray beam. WAXS was recorded at ambient temperature using 2θ scanning mode to an angle of 150°, using typically five data points per degree with a count time of 1 s. The data were fitted by modelling Gaussian peaks using the program SPECLOT.⁴⁸ The widths of the (111) peaks were related to crystallite size using the Scherrer equation.

HED. High-energy diffraction measurements were carried out on ESRF beamline ID15B,⁴⁹ with beam conditions of 6 GeV, 80 mA, and 2/3 filling mode using an X-ray energy of 89 keV, corresponding to a wavelength of 0.1393 Å. The beam size at the sample was 100 μm $\times$ 100 μm . The AAO membranes were mounted using a goniometer allowing their orientation to be varied by remote control, and studied face-on and edge-on to the X-ray beam, in air at ambient temperature. The two-dimensional diffraction patterns were collected on an image plate detector using typical data collection times of 20 min. They were radially integrated using the FIT2D software package⁵⁰ to display the intensity profiles as a function of the 2θ scattering angle. These profiles were fitted using a Rietveld method with the software package⁵¹ PowderCell 2.3. The mean crystallite sizes of the nanowires were determined using the Scherrer equation from the widths of the $\langle 111 \rangle$ peaks, measured by a least-squares fit of a Gaussian function.

SAXS and ASAXS. SAXS experiments were conducted on ESRF beamline ID01,⁴⁷ with beam conditions of 6 GeV, 200 mA, and 2/3 filling mode. The X-ray energy was typically 7610 eV, corresponding to a wavelength of 1.629 Å, or 8050 eV, corresponding to a wavelength of 1.540 Å. For ASAXS experiments on cobalt nanowires, X-ray energies of 7700 eV, 7718 eV and 7730 eV were additionally used, spanning the cobalt K-edge at 7709 eV. A typical beam size was 0.8 mm $\times$ 0.2 mm. A three-circle sample mounting system enabled the orientation of the AAO membrane samples relative to the X-ray beam to be varied by remote control. Measurements were

made in air at ambient temperature. The two-dimensional SAXS intensity patterns were measured either with a two-dimensional gas-filled detector (1024×1024 pixels each of $179 \mu\text{m} \times 179 \mu\text{m}$), or with a CCD detector (1242×1152 pixels each of $55 \mu\text{m} \times 55 \mu\text{m}$). A beamstop 6 mm in diameter masked the central area. The detectors were positioned at distances between 0.6 m and 4.5 m from the sample, giving a range for the scattering vector k of up to 3.0 nm^{-1} . Very high forward scattering intensity was observed from the empty and metal-filled AAO membranes. Typical counting times were 10 seconds or less. Background air-scattering counts were very low. The software package FIT2D⁵⁰ was used to background-correct the patterns and radially integrate them to display the intensity profiles as a function of the scattering angle or vector.

Results and discussion

Iron nanowires

Iron nanowires in AAO membranes have been studied by several groups using magnetic susceptibility measurements^{7,28,29,52–54} and Mössbauer spectroscopy.^{52,55,56} Although these nanowires are known to have the same bcc lattice as bulk iron (α -iron), their magnetic properties depend on diameter.

We have previously reported¹⁵ our structural work on iron nanowires in membranes with pores of diameter 12 nm and 24 nm. EXAFS showed them to be structurally very similar to bulk iron, but the XANES showed some differences from the bulk. HED showed that the Fe nanowires had a strong preferred orientation.

We have now extended this study to iron nanowires in AAO membranes with larger pore sizes (48 nm and 72 nm).

Possible oxidation must be a concern with nanowires of a metal such as iron. However, Mössbauer spectroscopy detected only small amounts of Fe(III), probably caused by partial oxidation at the pore ends, and showed that no further oxidation takes place even over long periods of time in air.⁵⁵ No evidence of oxidation could be found by introducing oxygen atoms into the lattice model in our EXAFS analysis.

The combined EXAFS results are summarised in Table 1. They confirm that the nanowires retain the bcc structure of bulk iron, and that the lattice parameter does not vary significantly with pore size. HED of the same samples, before they were pressed into pellets, confirmed their lattice symmetry and structural parameters. The iron nanowires have a preferred orientation with the [111] direction perpendicular to the pore axis; this is most marked in pores of smaller diameter. HED also showed that the individual crystallites in the nanowires are about 10 nm in diameter, appearing independent of pore size.

Although the iron nanowires are structurally almost identical to the bulk metal, their XANES shows a significant systematic variation with pore diameter (Fig. 2). As the pore size decreases, the broad peak close to the absorption edge, between 7.14 keV and 7.18 keV, is suppressed, and there is also a reduction in the intensity of the peak at 7.22 keV. However, the other features in the XANES remain almost unchanged. This is a strange observation, and at first we suspected it to be an artefact. However, we have now confirmed that the XANES spectra are fully reproducible with different Fe nanowire samples. The same effects are observed from samples in the form of membranes with aluminium backing, membranes with the backing removed, and the latter samples ground into pellets. Additionally, the results obtained on SRS beamline 7.1 and ESRF beamline BM29 are fully consistent with each other. Although we are unable to offer a full interpretation of this XANES behaviour, it is clear evidence that the electronic structure of the iron nanowires varies systematically with the pore diameter. This is all the more significant, because the EXAFS and HED analyses show that there is no systematic variation of interatomic distance or lattice parameter with pore size. So the implication is that the changing electronic structure of the nanowires depends directly on their diameter, and is not caused by a change in the lattice structure. This has major implications for understanding and controlling the physical and magnetic properties of the iron nanowires.

Cobalt nanowires

The magnetic properties of cobalt nanowires in AAO membranes have been studied by several groups.^{28,29,55,56}

Table 1 Representative results of Fe K-edge EXAFS refinements of iron nanowires. The results shown from ESRF BM29 are for a separately prepared series of samples; the results for the samples studied on SRS 7.1 were also confirmed on ESRF BM29. Data collection temperatures were 80 K at the SRS and 30 K at the ESRF^a

Synchrotron Sample form	Bulk iron	Fe-nanowires in 12 nm pores	Fe-nanowires in 24 nm pores	Fe-nanowires in 24 nm pores	Fe-nanowires in 12 nm pores	Fe-nanowires in 48 nm pores	Fe-nanowires in 72 nm pores
	SRS 7.1 4 μm foil	SRS 7.1 Stacked membranes with Al backing	SRS 7.1 Stacked membranes with Al backing	SRS 7.1 Pressed pellet	ESRF BM29 Pressed pellet	ESRF BM29 Pressed pellet	ESRF BM29 Pressed pellet
E_i/eV^b	–14.3 (6)	–4.0 (6)	–4.4 (6)	–6.1 (9)	–5.5 (9)	–4.8 (9)	–14 (1)
Lattice symmetry	bcc	bcc	bcc	bcc	bcc	bcc	bcc
$a_i/\text{\AA}^c$	2.857 (3)	2.857 (3)	2.856 (3)	2.858 (4)	2.863 (3)	2.859 (3)	2.863 (3)
N_i (fixed parameter) ^d	8*	8*	8*	8*	8*	8*	8*
$R_i/\text{\AA}^e$	2.474 (5)	2.474 (5)	2.473 (5)	2.475 (7)	2.480 (5)	2.476 (5)	2.480 (5)
A_1^f	0.005 (1)	0.007 (1)	0.006 (1)	0.008 (2)	0.001 (2)	0.001 (1)	0.005 (2)
A_2	0.007 (1)	0.007 (1)	0.006 (1)	0.006 (2)	0.004 (3)	0.002 (2)	0.010 (1)
A_3	0.009 (1)	0.008 (1)	0.008 (1)	0.009 (3)	0.006 (4)	0.004 (2)	0.011 (1)
A_4	0.009 (1)	0.012 (2)	0.012 (2)	0.010 (3)	0.002 (2)	0.001 (1)	0.005 (2)
A_5	0.010 (1)	0.010 (1)	0.009 (1)	0.010 (2)	—	—	—
A_6	0.010 (2)	0.012 (3)	0.011 (3)	0.012 (6)	—	—	—
R -factor (%)	28.4	29.7	27.9	32.4	27.1	21.2	24.2

^a Esd's in the final digits are given in brackets. ^b E_i = contribution of the wave vector of the zero photoelectron relative to the origin of k . ^c a = cell parameter. ^d N_i = number of atoms in the i th shell. ^e R_i = radial distance of atoms in the i th shell/ $\text{\AA}$. ^f A_i = Debye–Waller term of the i th shell ($A = 2\sigma^2$ with σ = Debye–Waller factor)/ $\text{\AA}^2$

Fig. 2 Fe K-edge XANES (ESRF BM29, fluorescence mode) for iron nanowires within AAO membranes with pores of different diameters. Two separately prepared samples with 12 nm pore size are shown; one (upper curve) was studied as a membrane with Al backing, the other (lower curve) as a pressed BN pellet. The XANES of bulk iron (foil, 4 μm thickness; recorded in transmission) is shown for comparison. The curves have been normalised to have the same absorption edge height, then shifted along the absorption axis for clarity.

Our initial structural study,¹⁵ using HED and EXAFS, showed that cobalt nanowires in AAO membranes of pore diameter 12 nm and 48 nm are a mixture of two different cobalt lattices: hcp and fcc. Both lattices showed preferred crystallographic orientation in the alumina pores. In bulk cobalt, the hcp structure (α -form) is found at room temperature, but the fcc structure (β -form) is stable only at temperatures above 417 °C.⁵⁷

The co-existence of two different lattices in AAO-supported cobalt nanowires had previously been concluded from X-ray diffraction²⁸ and NMR.⁵⁸ The latter study was on nanowires supported in commercial Anopore membranes and reported a different preferred lattice orientation, raising the possibility that this is sensitive to pore diameter and growth conditions. Mixed hcp : fcc lattices have also been found in cobalt nanowires supported in track-etched polycarbonate membranes, using X-ray diffraction^{59,60} and NMR⁶⁰ methods. It was reported that in polycarbonate pores of 50 nm diameter there was no indication of preferred lattice orientation,⁶⁰ and in larger pores of 100–400 nm diameter only the hcp lattice was detected by X-ray diffraction.^{61,62}

The proportion of fcc phase is of key importance. Mössbauer studies⁵⁶ suggested that the amount of fcc cobalt increases with decreasing nanowire diameter, and this appeared to be confirmed by our first HED study.¹⁵ The magnetic properties of these nanoscale materials will certainly be sensitive to lattice type, and the orientation of the *c*-axis and the magnetic axis within the pores are important issues. The regularity of pore filling by cobalt is also of importance.

Clearly, more detailed structural characterisation is essential for a full understanding of the magnetic properties of these materials.

In an attempt to characterise how the hcp : fcc ratio depends on pore size and nanowire growth conditions, we have now carried out further HED and EXAFS studies on cobalt nanowires within AAO membranes of a wider range of pore diameters, between 12 nm and 72 nm. For a matched set of membranes with 24 nm diameter pores, the cobalt nanowires were deposited at voltages of 10 V and 20 V as well as the usual 16 V. For a matched set of membranes with 48 nm diameter pores, the cobalt nanowires were additionally grown in an external magnetic field (0.35 T) applied in directions perpendicular and parallel to the pores.

It is difficult to distinguish hcp and fcc structures by EXAFS. The radial distribution functions of nearest and outer neighbours around the cobalt atoms are identical, unless in the hcp structure the *c/a* ratio varies from the ideal value, in which case the nearest-neighbour shell of coordination number 12 splits into two closely separated shells of six atoms each. Satisfactory EXAFS refinements with very similar *R*-values were obtained in both structures. For this reason, the hcp : fcc ratio was obtained from the HED measurements. The results are summarised in Table 2.

The hcp : fcc ratio does not depend linearly on the pore diameter. The preferred orientation of the hcp lattice is with the *c* axis is perpendicular to the main axis of the pores, and for the fcc lattice

Table 2 Representative results of high-energy diffraction measurements (ESRF beamline ID15B) of cobalt nanowires. The experiments to deposit nanowires at different voltages and in magnetic fields were carried out on AAO membranes prepared together as matched sets. Esd's are 0.002 Å in the cell parameters and 0.5 in the lattice type percentages

	Co-nanowires in 12 nm pores	Co-nanowires in 18 nm pores	Co-nanowires in 24 nm pores	Co-nanowires in 24 nm pores	Co-nanowires in 24 nm pores	Co-nanowires in 48 nm pores	Co-nanowires in 48 nm pores	Co-nanowires in 48 nm pores	Co-nanowires in 72 nm pores
Membrane growth voltage/V	10	15	20	20	20	40	40	40	60
Nanowire deposition voltage/V	16	16	10	16	20	16	16	16	16
Magnetic field <i>H</i>	None	None	None	None	None	None	0.35 T parallel to pores	0.35 T perpendicular to pores	None
% hcp cobalt	48.3	57.8	79.9	59.1	80.5	58.3	54.0	56.5	42.1
hcp <i>a</i> -cell/Å	2.5196	2.5160	2.5136	2.5202	2.5242	2.5177	2.5082	2.5191	2.5068
hcp <i>c</i> -cell/Å	4.0820	4.0981	4.0979	4.0731	4.0968	4.0908	4.1128	4.1268	4.0749
% fcc cobalt	51.7	42.2	20.1	40.9	19.5	41.7	46.0	43.5	57.9
fcc <i>a</i> -cell/Å	3.5539	3.5527	3.5405	3.5488	3.5559	3.5507	3.5457	3.5572	3.5404

the [111] direction perpendicular to the main axis. These conclusions revise those of our previous study. The size of the individual crystallites in the nanowires, for both the hcp and fcc structures, is close to 10 nm for pore diameters up to 24 nm, and increases to 20 nm for 48 nm and 72 nm diameter pores. Growth of the nanowires in the magnetic field, and the variation of the electrochemical AC plating voltage, has a very limited effect on the structure. The only possibly statistically significant effect is a slight increase in the c-axis cell parameters of the hcp form for the wires grown in magnetic fields of 0.35 T. In contrast, it was previously reported that magnetic fields of less than 0.05 T significantly influenced the growth of cobalt nanowires in polycarbonate membranes of 400 nm pore diameter.⁶²

It is disappointing to find no clear correlations between the cobalt nanowire growth conditions and the relative proportions of hcp and fcc lattices in the nanowires. It will be important to synthesise cobalt nanowires with controlled structure if their properties are to be successfully exploited. It has been suggested⁶⁰ that formation of the fcc phase is promoted by rapid electrochemical deposition, because fast nanowire growth causes tensile stress in the lattice. The pH of the solution from which the cobalt is deposited is another important variable.⁶³

The longer-range structural ordering of these cobalt nanowire assemblies is of key importance in understanding their ferromagnetic properties. For example, if not all the pores are filled with cobalt, is the distribution of filled pores random or spontaneously organised into a superlattice? We have used SAXS and ASAXS to investigate the mesoscopic ordering of the pores and their filling by cobalt.

The empty AAO membranes give two-dimensional SAXS intensity profiles which are very sensitive to sample alignment.³² A ring structure was observed for channels parallel to the X-ray beam. Rotation of the plane of the membrane changed the pattern through a complex sequence to a set of vertical spots for channels perpendicular to the beam. Similar patterns have been observed in small-angle neutron scattering studies of commercial AAO membranes.⁶⁴

The SAXS intensity profiles are a convolution of a cylinder form factor for individual pores and a two-dimensional structure factor for the hexagonal array of parallel channels. The integrated intensity profiles in *k*-space showed regular oscillatory patterns varying systematically with anodic deposition voltage. The positions of the intensity maxima are interpreted as pseudo-Bragg peaks arising from the hexagonal array of pore axes. The first peak position corresponds to a spatial dimension representing the mean separation of the pore axes, confirming the linear relationship between voltage and pore separation.³²

AAO membranes are a two-phase medium; their SAXS amplitude function depends on the electron density contrast of the alumina matrix and the empty pores. If the pores are filled with a material with the same electron density as the host matrix, the scattering intensity will be zero. This technique of “contrast matching” has attracted substantial attention in the context of filling porous solids with liquids.⁶⁵ Nanowires of metals have electron densities too high to give a contrast match with alumina. However, the electron density of cobalt is approximately double that of alumina, so the contrast values for alumina/void and alumina/cobalt are of opposite sign but close in magnitude.³³ If cobalt completely fills the pore cavities, the shape of the intensity profile should therefore be unchanged from that of the empty membrane. Any deviations will contain information on the regularity of pore-filling, as voids in the filling medium convert the assembly to a three-phase system.

We previously reported³³ that the SAXS intensity profile from a cobalt-filled AAO membrane with pore diameter 48 nm was modified compared with that from an empty membrane. We have now extended this study to pore diameters between 12 nm and 170 nm. Matched samples were prepared for each pore size, and one membrane of each pair was filled with cobalt. Our initial result is confirmed. Fig. 3 compares the SAXS intensity profiles of cobalt-filled and empty membranes with 24 nm diameter pores. The peaks from the cobalt-filled membrane are displaced to slightly different *k*-values, and the oscillatory amplitude is reduced. This increased disorder in the SAXS profiles suggests that the distribution of the cobalt does not correspond precisely to the void volume of the empty pores. Some nanowires may be discontinuous, or there may be some empty pores. Further data analysis is in progress.

We previously pointed out³³ that absorption effects, which are usually neglected in the SAXS formalism, may be important for this membrane system. Evidence for this is given by the attenuation of the SAXS profiles which we have observed from thicker membranes,³² and in

Fig. 3 SAXS intensity profile from a cobalt-filled AAO membrane with 24 nm pore diameter, compared with that from a matched empty membrane with the same pore size. The membranes were face-on to the X-ray beam.

subsequent experiments with stacking layers of membranes. To study this idea, and isolate the scattering contribution of the cobalt in more detail, we have carried out an anomalous scattering experiment (ASAXS). 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 cobalt K-absorption edge, there are subtle changes to the shapes of the peaks in the scattering profiles.

This part of our study is at an early stage. A full analysis of the ASAXS patterns should enable the contribution of the cobalt atoms to the SAXS pattern to be separated, and the extent of pore filling to be evaluated in more detail. This is necessary for a quantitative interpretation of the ferromagnetic properties of these nanowires.

Tin nanowires

Tin exists in the bulk two structural phases: tetragonal β -tin ("white tin"), stable above 13.2 °C, and cubic α -tin ("grey tin"). The transition in between these phases shows a large temperature hysteresis because of the large volume change involved in the transition.⁶⁶ Additionally, tin is superconducting at very low temperatures ($T_c = 3.7$ K). Interestingly, the phase that shows superconductivity is tetragonal β -tin, which is metastable at low temperatures.

Tin nanowires are therefore a prime candidate for study, to see if their confinement in the pores of AAO membranes modifies their structural and physical properties. We have studied tin nanowires in pores between 12 nm and 72 nm in diameter. This is the first study of Sn nanowires in AAO membranes.

The EXAFS results show only the presence of the tetragonal β -structure at ambient temperature and also at 80 K. An attempt to induce a phase change in the tin nanowire/AAO samples (24 nm pore diameter) by storage at low temperatures (−10 °C for 24 hours) did not result in any change at all to the EXAFS spectra. This is not too surprising, because the large volume expansion involved in the phase change from β -tin to α -tin makes it kinetically very slow.⁶⁶

The HED results at room temperature confirm the tetragonal β -structure. There is some preferred orientation of the c-axis perpendicular to the pores, and this is strongest in the smallest pore diameters (Fig. 4).

Initial magnetic susceptibility measurements⁴⁰ show that tin nanowires in AAO pores of 12 nm diameter become superconducting at the same temperature as bulk tin: 3.7 K. A more detailed account of their magnetic properties will be published elsewhere.⁶⁷

Gallium nitride nanowires

Gallium nitride (GaN) is a wide bandgap (3.45 eV) semiconductor which is under intense study for prospective applications in optoelectronic devices in the blue and ultraviolet wavelengths, and in

Fig. 4 High-energy X-ray diffraction pattern for tin nanowires in AAO membranes with 48 nm pore diameter. The membrane was edge-on to the X-ray beam.

other high-performance electronic devices^{68,69} Several thousand papers devoted to the study of this material have been published in the past ten years.

Nanowires of GaN in mesoporous alumina have been studied as a possible basis for transparent optoelectronic devices. These GaN nanowires have previously been prepared by reaction of Ga_2O_3 vapour with ammonia at 1000°C ,¹⁸ or by direct reaction of Ga vapour with ammonia at 960°C .⁷⁰ They are reported from X-ray diffraction to have the hexagonal wurtzite structure,¹⁸ although a cubic zinc blende structure is also possible and has been observed in thin films of GaN.⁷¹

We prepared our GaN nanowires^{16,41} by depositing gallium nitrate in 20 nm diameter pores from aqueous solution, and thermolysing at 1000°C to form Ga_2O_3 , which was reacted with ammonia at 1000°C or 1150°C . The photoluminescence spectra of these GaN/AAO nanowires prepared at 1000°C have been reported.¹⁶ The samples prepared at 1150°C showed increased luminescence.⁴¹ As our synthetic route is new, it is especially important to verify the composition of the nanowires and characterise their structure, especially for those prepared at 1150°C , which is higher than the temperature normally used.

Gallium K-edge EXAFS data from the samples prepared at 1000°C refined satisfactorily in the hexagonal wurtzite structure. There was no significant difference between results from the membranes which had been filled once and five times with gallium nitrate. However, for the samples prepared at 1150°C the structural refinement in this model was less satisfactory. The fit to the experimental data was substantially improved by introducing aluminium atoms into the model, substituting for a proportion of the gallium atoms in the lattice. These findings were confirmed by the HED results. The samples prepared at 1000°C showed diffraction patterns entirely consistent with pure GaN in the wurtzite structure (Fig. 5), with some preferred orientation of the *c*-axis perpendicular to the pore axis. For the samples prepared at 1150°C , close inspection of the integrated diffraction pattern showed a doubling of the main peaks. We interpret this as showing the presence of a $\text{Ga}_x\text{Al}_{1-x}\text{N}$ solid solution. The change in the unit cell volume derived from the diffraction pattern was used to calculate the proportion of aluminium in this phase as being up to 40%; this agreed with the value obtained from the EXAFS refinements. The sample that had been filled five times with gallium nitrate and treated at 1150°C also showed HED peaks corresponding to a separate AlN phase.

Clearly, the use of a temperature of 1150°C for the preparation of the GaN nanowires has led to migration of aluminium from the host membrane into the nanowire lattice. The conclusion is that temperatures above 1000°C must not be used in preparation of this type of GaN nanowire material. As an additional complication, the HED patterns showed that AAO

Fig. 5 High-energy X-ray diffraction pattern for gallium nitride nanowires in AAO membranes with 24 nm pore diameter. The membrane was edge-on to the X-ray beam.

membranes heated to these high temperatures contain a proportion of crystalline γ -alumina and α -alumina.

Finally, we point out that these gallium nitride nanowires are of great potential interest for study by SAXS. The electron density of GaN is almost equal to that of Al_2O_3 , making the two materials an excellent contrast match. The SAXS pattern of the GaN nanowires will therefore give a way to directly measure the extent of pore filling, calculate the proportion of voids in the pores, and characterise any long-range order in the filling pattern.

Conclusion

Our philosophy is that detailed characterisation of the structures of assemblies of metal and semiconductor nanowires within AAO membranes is an essential prerequisite to understanding and controlling their physical properties. We have studied their structures on a variety of length scales using a powerful combination of complementary methods, each based on the use of synchrotron radiation X-rays. Of particular note is our use of high-energy X-ray diffraction, which achieves direct structural study of nanowire anisotropy within the alumina pores.

In this paper we have reported our studies of four different nanowire/AAO systems: the ferromagnetic metals iron and cobalt, the superconducting metal tin, and the semiconductor gallium nitride. Although their structures are very similar to those of the corresponding bulk materials, in each case aspects of our results give new insight into their properties. The electronic properties of iron nanowires have been shown by XANES to depend on nanowire diameter. We have confirmed the co-existence of two different lattice structures in cobalt nanowires, although the hcp : fcc ratio does not show a clear relationship to pore size or nanowire preparation conditions. Iron, cobalt and tin nanowires have all been shown to grow in the pores with preferred lattice orientations; in the case of iron and tin the preference is greater in the smaller pores. We have characterised the structures of gallium nitride nanowires prepared by a new route and shown the importance of temperature control during the syntheses.

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References

- 1 F. Keller, M. S. Hunter and D. L. Robinson, *J. Electrochem. Soc.*, 1953, **100**, 411.
- 2 J. W. Diggle, T. C. Downie and C. W. Goulding, *Chem. Rev.*, 1969, **69**, 365.
- 3 J. P. O'Sullivan and G. C. Wood, *Proc. R. Soc. London, Ser. A*, 1970, **317**, 511.
- 4 Anopore membranes; marketed by Whatman International Limited, Maidstone, Kent, England.
- 5 G. Hornyak, M. Kröll, R. Pugin, T. Sawitowski, G. Schmid, J.-O. Bovin, G. Karsson, H. Hofmeister and S. Hopfe, *Chem. Eur. J.*, 1997, **3**, 1951.
- 6 T. Hanaoka, H.-P. Kormann, M. Kröll, T. Sawitowski and G. Schmid, *Eur. J. Inorg. Chem.*, 1998, 807.
- 7 D. AlMawlawi, N. Coombs and M. Moskovits, *J. Appl. Phys.*, 1991, **70**, 4421.
- 8 C. R. Martin, *Science*, 1994, **266**, 1961.
- 9 C. A. Huber, T. E. Huber, M. Sadoqi, J. A. Lubin, S. Manalis and C. B. Prater, *Science*, 1994, **263**, 800.
- 10 D. Routkevitch, A. A. Tager, J. Haruyama, D. AlMawlawi, M. Moskovits and J. M. Xu, *IEEE Trans. Electron Devices*, 1996, **43**, 1646.
- 11 J. C. Hulthen and C. R. Martin, *J. Mater. Chem.*, 1997, **7**, 1075.
- 12 T.-A. Hanaoka, A. Heilmann, M. Kröll, H.-P. Kormann, T. Sawitowski, G. Schmid, P. Jutzi, A. Klipp, U. Kreibitz and R. Neuendorf, *Appl. Organomet. Chem.*, 1998, **12**, 367.
- 13 M. Sun, G. Zangari, M. Shamsuzzoha and R. M. Metzger, *Appl. Phys. Lett.*, 2001, **78**, 2964.
- 14 R. E. Benfield, D. Grandjean, R. Pugin, T. Sawitowski, M. Kröll and G. Schmid, *J. Phys. Chem. B*, 2001, **105**, 1961.
- 15 R. E. Benfield, D. Grandjean, J. C. Dore, Z. Wu, T. Sawitowski, M. Kröll and G. Schmid, *Eur. Phys. J. D*, 2001, **16**, 399.
- 16 G. Schmid, *J. Mater. Chem.*, 2002, **12**, 1231.
- 17 D. Routkevitch, T. Bigioni, M. Moskovits and J. M. Xu, *J. Phys. Chem.*, 1996, **100**, 14037.
- 18 G. S. Cheng, L. D. Zhang, Y. Zhu, G. T. Fei, L. Li, C. M. Mo and Y. Q. Mao, *Appl. Phys. Lett.*, 1999, **75**, 2455.
- 19 J. K. Lee, W. K. Koh, W. S. Chae and Y. R. Kim, *Chem. Commun.*, 2002, 138.
- 20 T. Kyotani, B. K. Pradhan and A. Tomita, *Bull. Chem. Soc. Jpn.*, 1999, **72**, 1957.
- 21 C. W. Wang, M. K. Li, S. L. Pan and H. L. Li, *Chin. Sci. Bull.*, 2000, **45**, 1373.
- 22 Cyclopore and Nuclepore membranes; marketed by Whatman International Limited, Maidstone, Kent, England.
- 23 Q. M. Zhang, Y. Li, D. S. Xu and Z. N. Gu, *J. Mater. Sci. Lett.*, 2001, **20**, 925.
- 24 J. A. Creighton and D. G. Eadon, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 3881.
- 25 C. A. Foss, G. L. Hornyak, J. A. Stockert and C. R. Martin, *J. Phys. Chem.*, 1994, **98**, 2963.
- 26 S. L. Pan, D. D. Zeng, H. L. Zhang and H. L. Li, *Appl. Phys. A*, 2000, **70**, 637.
- 27 T. R. Gao, Z. Y. Chen, Y. Peng and F. S. Li, *Chin. Phys.*, 2002, **11**, 1307.
- 28 D. J. Sellmyer, M. Zheng and R. Skomski, *J. Phys. Condens. Matt.*, 2001, **13**, R433.
- 29 R. M. Metzger, V. V. Konovalov, M. Sun, T. Xu, G. Zangari, B. Xu, M. Benakli and W. D. Doyle, *IEEE Trans. Magn.*, 2000, **36**, 30.
- 30 B. R. Martin, D. J. Dermody, B. D. Reiss, M. M. Fang, L. A. Lyon, M. J. Natan and T. E. Mallouk, *Adv. Mater.*, 1999, **11**, 1021.
- 31 F. S. Li and L. Y. Ren, *Phys. Status Solidi A*, 2002, **193**, 196.
- 32 R. E. Benfield, D. Grandjean, J. C. Dore, M. Kröll, G. Schmid and D. Le Bolloc'h, submitted for publication.
- 33 J. C. Dore, R. E. Benfield, D. Grandjean, G. Schmid, M. Kröll and D. Le Bolloc'h, *Stud. Surf. Sci. Catal.*, 2002, **144**, 163.
- 34 *X-Ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS and XANES*, ed. D. C. Koningsberger and R. Prins, Wiley, New York, 1988.
- 35 C. C. Tyson, A. Bzowski, P. Kristof, M. Kuhn, R. Sammynaiken and T. K. Sham, *Phys. Rev. B*, 1992, **45**, 8924.
- 36 *Small Angle X-ray Scattering*, ed. O. Glatter and O. Kratky, Academic Press, London, 1982.
- 37 D. C. Bazin, D. A. Sayers and J. J. Rehr, *J. Phys. Chem.*, 1997, **101**, 11040.
- 38 A. Benedetti, L. Bertoldo, P. Canton, G. Goerigk, F. Pinna, P. Riello and S. Polizzi, *Catal. Today*, 1999, **49**, 485.

- 39 T. Sawitowski, PhD thesis, University of Essen, 1999.
- 40 M. Kröll, PhD thesis, University of Essen, 2000.
- 41 M. Geerkens, PhD thesis, University of Essen, 2002.
- 42 SRS website: http://srs.dl.ac.uk/XRS/Stations/Descriptions/stat7_1.html.
- 43 SRS website: http://srs.dl.ac.uk/XRS/Stations/Descriptions/stat9_2.html.
- 44 ESRF website: http://www.esrf.fr/exp_facilities/BM29/.
- 45 N. Binsted, J. W. Campbell, S. J. Gurman and P. C. Stephenson, *EXAFS Analysis Programs*, Daresbury Laboratory, Warrington, 1991.
- 46 The United Kingdom Chemical Database Service, D. A. Fletcher, R. F. McMeeking and D. Parkin, *J. Chem. Inf. Comput. Sci.*, 1996, **36**, 746.
- 47 ESRF website: http://www.esrf.fr/exp_facilities/ID1/user_guide/.
- 48 V. Neupert, S. Peters and V. Rey, *SPECPLLOT*, ESRF Grenoble, 1998.
- 49 ESRF website, www.esrf.fr/exp_facilities/ID15B/home/id15home.html.
- 50 A. P. Hammersley, *FIT2D: An Introduction and Overview*. ESRF Internal Report ESRF97HA02T, 1997.
- 51 W. Kraus and G. Nolze, *PowderCell 2.3*, Bundesanstalt für Materialforschung und -prüfung, Berlin, 2002, http://www.bam.de/service/publikationen/powdercell_i.htm.
- 52 Y. Peng, H. L. Zhang, S. L. Pan and H. L. Li, *J. Appl. Phys.*, 2000, **87**, 7405.
- 53 K. H. Lee, H. Y. Lee, W. Y. Jeung and W. Y. Lee, *J. Appl. Phys.*, 2002, **91**, 8513.
- 54 T. G. Sorop, C. Untiedt, F. Luis, M. Kröll, M. Rasa and L. J. de Jongh, *Phys. Rev. B*, 2003, **67**, 014402.
- 55 P. Paulus, F. Luis, M. Kröll, G. Schmid and L. J. de Jongh, *J. Magn. Magn. Mater.*, 2001, **224**, 180.
- 56 M. Kröll, W. J. Blau, D. Grandjean, R. E. Benfield, F. Luis, P. Paulus and L. J. de Jongh, *J. Magn. Magn. Mater.*, 2002, **249**, 241.
- 57 N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon, Oxford, 1984, p. 1292.
- 58 G. J. Strijkers, J. H. J. Dalderop, M. A. A. Broeksteeg, H. J. M. Swagten and W. J. M. de Jonge, *J. Appl. Phys.*, 1999, **86**, 5141.
- 59 A. Fert and L. Piraux, *J. Magn. Magn. Mater.*, 1999, **200**, 338.
- 60 V. Scarani, B. Doudin and J. P. Ansermet, *J. Magn. Magn. Mater.*, 1999, **205**, 241.
- 61 A. K. M. Bantu, J. Rivas, G. Zaragoza, M. A. López-Quintela and M. C. Blanco, *J. Appl. Phys.*, 2001, **89**, 3393.
- 62 S. H. Ge, C. Li, X. Ma, W. Li, L. Xi and C. X. Li, *J. Appl. Phys.*, 2001, **90**, 509.
- 63 A. Encinas, M. Demand, J.-M. George and L. Piraux, *IEEE Trans. Magn.*, 2002, **38**, 2574.
- 64 D. Marchal, C. Bourdillon and B. Demé, *Langmuir*, 2001, **17**, 8313.
- 65 D. W. Hua, J. V. D'Souza, P. W. Schmidt and D. M. Smith, *Stud. Surf. Sci. Catal.*, 1994, **87**, 255.
- 66 N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon, Oxford, 1984, pp. 433–4.
- 67 M. Kröll, W. J. Blau, T. G. Sorop and L. J. de Jongh, in preparation.
- 68 G. Fasol, *Science*, 1996, **272**, 1751.
- 69 F. A. Ponce and D. P. Bour, *Nature*, 1997, **386**, 351.
- 70 J. Zhang, X. S. Peng, X. F. Wang, Y. W. Wang and L. D. Zhang, *Chem. Phys. Lett.*, 2001, **345**, 372.
- 71 M. Katsikini, H. Rossner, M. Fieber-Erdmann, E. Holub-Krappe, T. D. Moustakas and E. C. Paloura, *J. Synchrotron Radiat.*, 1999, **6**, 561.
- 72 EU TMR network CLUPOS: network homepage <http://www.clupos.lth.se>.