EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

http://193.49.43.2:8080/smis/servlet/UserUtils?start

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Structural Studies of Core-Shell Heterostructured Nanocables	**Experiment number**: CH 2052
Beamline: BM 26A	**Date of experiment**: from: 02 September 2005 to: 09 September 2005	**Date of report**: 14/11/05
Shifts: 18	**Local contact(s)**: Dr Serge Nikitenko	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Dr Justin Holmes (University College Cork)

Dr Donna Arnold (University College Cork)*

Dr Andrew Beale (University of Utrecht)

Mr Brian Daly (University College Cork)*

Mr Jaideep Kulkarni (University College Cork)

Dr John Hanrahan (University College Cork)*

Miss Machteld Van der Meulen (University College Cork)*

Report:

We have synthesised high density arrays of cobalt/germanium (Co/Ge) and magnetite/germanium (Fe_3O_4/Co) coaxial nanocables within the channels of porous anodic aluminium oxide (AAO). Electron microscopy studies have shown that the coaxial nanocables formed consist of a semiconducting core surrounded by a discrete ferromagnetic sheath. Magnetic analysis of the Co/Ge nanocables have shown them to be ferromagnetic Curie temperature (T_c) ~ 260 K. This ferromagnetism does not result from the cobalt layer alone but is intrinsic to the Co/Ge heterostructure. To fully understand these nanocables we conducted EXAFS/XANES experiments in transmission mode using beamline BM26A on the following core:shell materials, Co shell – Ge Core, Co shell – Fe_3O_4 Core and Fe_3O_4 shell – Co Core respectively. In this report we have discussed specifically the data collected for the Co shell, Ge core heterostructured material. However, analysis of all experimental data collected for these core-shell heterostructured materials showed excellent correlations between the experimentally observed data and their respective theoretical models confirming the core-shell nature of these structures.

Co shell: Fitting of the EXAFS data yeilded very good correlations between the experimental data and the theoretical shell model (figure 1(a) and (c)). This data clearly shows the Co to adopt primarily the hexagonal close packed structure (hcp) but also indicates the precence of small amounts of Co with the cubic structure. A small amount of Co – O can be seen which is consistent with the interface between the Co shell and the AAO template material. All remaining peaks can be attributed to Co – Co neighbours. There is no evidence in the EXAFS for a Co – Ge environment this can be explained by the fact that the Co – Ge interface has a very small surface area in comparison to the Co – O interface and as such the contribution would be very small. Additionally the approximate bond length for Co – Ge is ~ 2.49 Å and would effectively be masked by the much larger Co – Co contributions at 2.5 Å.

Ge core: As with the Co EXAFS data collected at the Ge K-edge good correlation between the experimental data and the theoretical model is observed (figure 1(b) and (d)). All peaks can be attributed to Ge – Ge neighbours. As at the Co K-edge there is no evidence in the EXAFS for a Co – Ge environment and as with

Co this contribution would effectively be masked by the much larger Ge – Ge bonding contributions at 2.45 Å. However, since we are unable to see any contribution from the Co – Ge interface we can suggest that the interactions between Ge and Co is discrete, limited only to the interface with no extended formation of Co – Ge alloys as a result of Ge migration into the Co lattice during the synthesis of the core material.

From these experiments and comparison of the observed data with that collected for standard materials in identical experimental conditions we can clearly see that there is no evidence for the formation of any germanium oxide or cobalt oxide materials confirming that there is no interaction between the AAO membrane and the Ge does indeed form a core material within the Co shell and that there is no oxide formation on the inside of the Co shell prior to the Ge core experiments consistent with the XRD and TEM experiments.

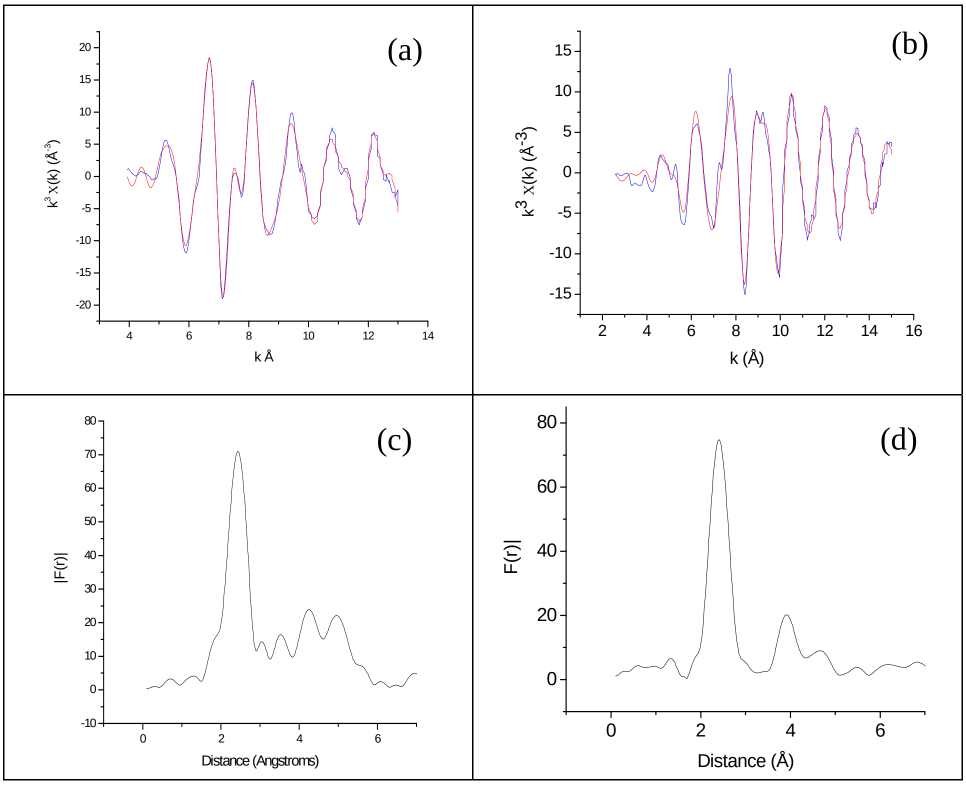

Figure 1: Typical experimental $k^3\chi(k)$ *and the corresponding theoretical fit for (a) Co K-edge and (b) Ge K-edge and absolute values of fourier transform of* $k^3\chi(k)$ *into r space for (c)Co K-edge and (d) Ge K-edge for the Co shell Ge core heterostructures.*

The effects of annealing temperature on these structures was also investigated by collecting EXAFS data for all material annealed at 650, 800 and 950 ^{O}C. These materials clearly showed differences to the as synthesised materials and when fitted exhibit increasing amounts of alloy formation consistent with the results seen by XPS and XRD investigations.

In conclusion experiments conducted at the ESRF clearly emphasise the power of EXAFS to investigate the structural environment of core:shell heterostructures. These results clearly demonstrate the formation of Ge-Co, Co-Fe$_3$O$_4$, and Fe$_3$O$_4$-Co core:shell materials which exhibit discrete interactions at the interfaces. These results show no evidence for the formation of Co-Ge alloys or oxide materials in the as synthesised materials further confirming that the unique magnetic properties observed do not originated from undesired second phases but from the complex interactions between the core and shell. This is further confirmed from the data collected for these materials annealed at high temperature where alloy formation is evident. These experiments have been essential in understanding the complex structural and magnetic interactions exhibited by these systems.