ESRF	**Experiment title:** Atomic Structure in Composite Magnetic Core/Shell Nanoclusters	**Experiment number**: HE-3224
Beamline: BM29	**Date of experiment**: from: 29/01/10 to: 02/02/10	**Date of report**: 16/03/10
Shifts:12	**Local contact(s)**: Matthieu Chorro	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Dr S.H.Baker * University of Leicester, UK

Dr M.Roy* University of Leicester, UK

Mr M. Qureshi * University of Leicester, UK

Background and Experimental

It is well established that novel behaviour in magnetic nanosized clusters arises in part due to an enhanced proportion of under-coordinated surface atoms. However the atomic structure in nanoclusters also plays a critical role in determining their magnetic properties; indeed, it is possible to "engineer in" different magnetic properties by forcing the clusters to adopt different atomic structures, by embedding them in a matrix of a different material for example [1,2]. Such atomic engineering also offers exciting prospects for new types of cluster, such as magnetic core/shell clusters comprising a magnetic core surrounded by a shell of another material. Potential applications are far-reaching, and include *in vivo* biomedical applications as well as enhanced data recording and storage. Here we report on atomic structure in magnetic Fe/Cu and Fe/Au core/shell clusters, prepared directly by gas-phase deposition.

Using a technique recently developed by us, films of Fe/Cu and Fe/Au core/shell nanoclusters were deposited *directly* from the gas phase onto Si(100) substrates. In brief a beam of Fe nanoclusters, ~ 2 nm in diameter and produced by a gas aggregation source [3], passes through a hot cell containing vapour of the shell material. The shell thickness is controlled by the vapour pressure, and hence temperature, of the coating cell. Atomic structure in the core/shell clusters was determined by means of Fe K edge and Cu K edge EXAFS experiments on BM29. The measurements were performed using fluoresence detection. Spectra free from diffraction "glitches" were obtained thanks to use of a rotating sample holder. The spectra were background subtracted using the PySpline program and analysed using the EXCURV98 program.

Results for Fe/Cu Core/Shell Clusters

Fig.1 shows Fe K edge spectra χ, weighted by k^3, and associated Fourier transforms for (i) an Fe MBE film (ii) an Fe/Cu core/shell cluster film for which the vapour pressure of Cu during deposition was 1.6×10^{-4} mbar (iii) an Fe/Cu core/shell cluster film for which the Cu vapour pressure was 1.1×10^{-3} mbar. A 5-shell fit, entirely consistent with the b.c.c. structure, was obtained for the Fe MBE film. The nearest-neighbour

interatomic distance obtained in the fit of 2.47 ± 0.01 Å implies a lattice parameter of 2.85 ± 0.02 Å (c.f. 2.87 Å in bulk Fe). The EXAFS for the 1.6×10^{-4} mbar Fe/Cu cluster film looks qualitatively similar to that for the Fe MBE film, and indeed a 5-shell fit consistent with b.c.c. is obtained yielding a nearest-neighbour distance of 2.48 ± 0.01 Å (and hence lattice parameter of 2.86 ± 0.02 Å). For the 1.1×10^{-3} mbar Fe/Cu cluster film, the EXAFS looks qualitatively different, and in fact similar to that measured by us for f.c.c. Fe clusters embedded in a Cu matrix [2]. A single shell fit yields a nearest neighbour distance of 2.51 ± 0.01 Å which implies an f.c.c. lattice parameter of 3.55 ± 0.02 Å, slightly shorter than (although consistent within error with) the value of 3.58 ± 0.02 Å measured by us previously for f.c.c. Fe clusters [2]. Higher shells are weakly defined, consistent with a certain amount of disorder. The atomic ratios Fe/Cu for the 1.6×10^{-4} mbar and 1.1×10^{-3} mbar films (obtained from SEM analysis) are 0.69 and 8.19 respectively. Since about 40% of the Fe atoms in the 2nm Fe cores reside at the Fe core surface, this implies that the Cu shell thicknesses are ~ 1.7 and 20.5 monolayers (ML) respectively. So shell thicknesses of ~ 2 ML of Cu are not sufficient to drive the structural change in the Fe core from b.c.c. to f.c.c.; increasing the shell thickness to 20 ML is sufficent to achieve this.

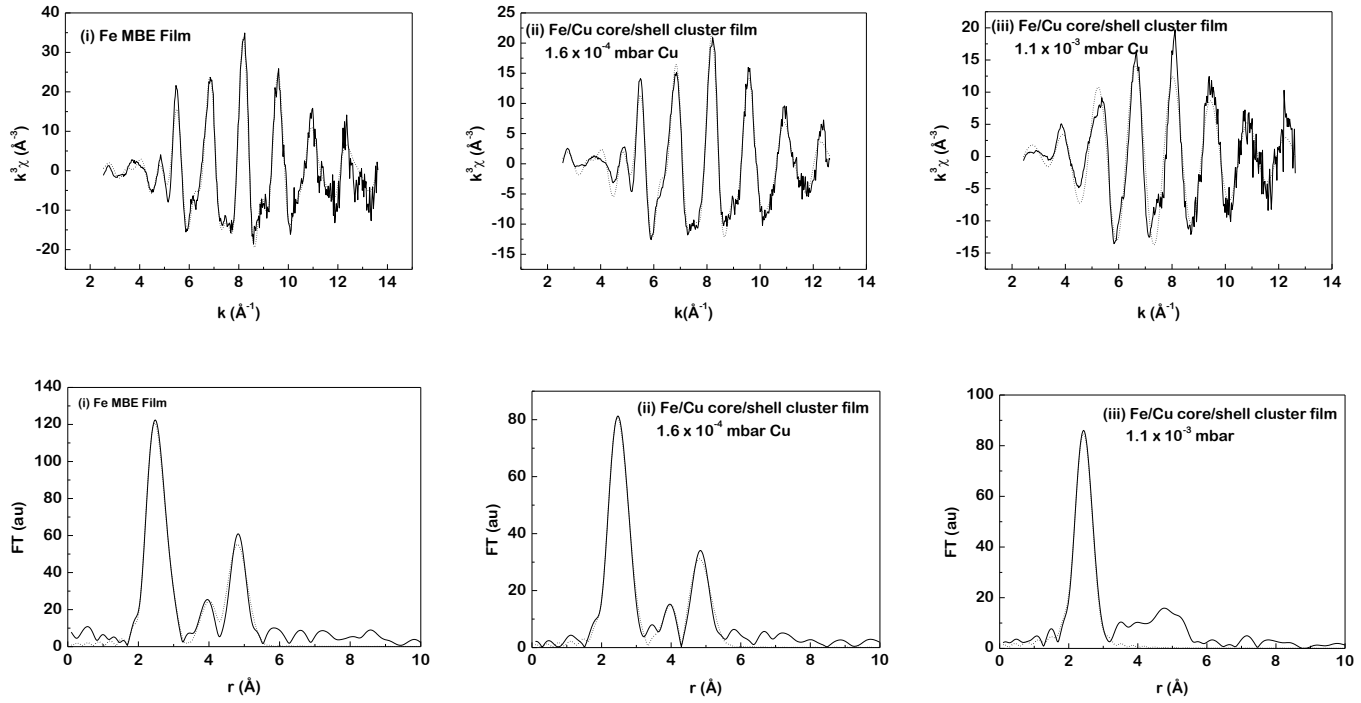

Figure 1 Fe K edge spectra for Fe/Cu films. Full lines – data; dashed lines – fit.

Fig. 2 shows the Cu K edge EXAFS, $k^3\chi$, and associated Fourier transforms for (i) a Cu MBE film (ii) the Fe/Cu core/shell cluster film for which the Cu vapour pressure during deposition was 1.1×10^{-3} mbar (iii) the Fe/Cu core/shell cluster film for which the Cu vapour pressure was 1.6×10^{-4} mbar. A 4-shell fit, entirely consistent with the f.c.c. structure, was obtained for the Cu MBE film data; the fit gave a nearest neighbour distance of 2.54 ± 0.01 Å and, hence, lattice parameter of 3.59 ± 0.02 Å (c.f. 3.61 Å in bulk Cu). The EXAFS for the 1.1×10^{-3} mbar Fe/Cu film looks qualitatively similar to that for the Cu MBE film, and indeed analysis of the data yields an f.c.c. fit with nearest neighbour distance identical to that in the Cu MBE film. Hence, the 20 ML Cu shell has the same structure as bulk Cu. For the 1.6×10^{-4} mbar Fe/Cu film, the EXAFS looks different. Single shell analysis yields 6.8 ± 0.5 atoms at an interatomic distance of 2.48 ± 0.01 Å. (Higher shells are very poorly defined). The fit distance obtained is identical to the nearest neighbour distance obtained for the b.c.c. Fe core in this sample, indicating that atoms in the 1.7 ML Cu shell sit epitaxially on the surface of the Fe core.

Results for Fe/Au Core/Shell Clusters

Fe K edge EXAFS spectra for measured for the Fe/Au core/shell cluster films looked qualitatively similar to that for the Fe MBE film (see fig.1). Analysis of the data confirms this and in all cases yields fits that are consistent with a b.c.c. structure in the Fe cores, although with a stretch in lattice parameter relative to the bulk Fe value. Fe/Au cluster films prepared with Au vapour pressures of 6.2×10^{-5} mbar and 2.1×10^{-4} mbar,

corresponding to shell thicknesses of ~ 1.8 ML of Au and ~ 1 ML of Au respectively, have nearest-neighbour distances of 2.52 ± 0.02 Å and 2.50 ± 0.01 Å respectively; this yields lattice parameters of 2.91 ± 0.03 Å and 2.89 ± 0.02 Å respectively (c.f. 2.87 Å for the bulk b.c.c. Fe value, and 2.85 ± 0.02 Å measured for the Fe MBE film). In the case of a film containing 6.6% filling fraction of Fe clusters in a Au matrix (effectively the limiting case of very thick Au shells), the nearest neighbour distance obtained was 2.52 ± 0.01 Å which gives a b.c.c lattice parameter of 2.91 ± 0.02 Å. There is also evidence for a degree of static disorder in the Fe cores. The Debye-Waller factors $2\sigma^2$ (for nearest neighbours) obtained in the fits are 0.025 ± 0.002 Å^2, 0.019 ± 0.002 Å^2, and 0.024 ± 0.002 Å^2, for the 6.2 × 10^{-5} mbar Fe/Au film, the 2.1 × 10^{-4} mbar Fe/Au film, and 6.6% Fe cluster/Au matrix film respectively; these values are larger than the figure of 0.009 ± 0.001 Å^2 measured for the Fe MBE film. There does not appear to be any appreciable amount of alloying at the core/shell interface – Fe K edge EXAFS measured for an $Fe_{0.10}Au_{0.90}$ alloy film grown by MBE looked very different, the analysis indicating an f.c.c. structure for this sample.

Summary

It is clear that atomic structure in the Fe cores of Fe-core/shell nanoclusters is strongly influenced by the surrounding shell. In the case of Fe/Cu clusters, a thick enough Cu shell can drive in a structural change from b.c.c. to f.c.c. in the Fe core, while for Fe/Au clusters the core structure remains b.c.c. but with significant stretching of lattice parameter. Both these effects will critically affect magnetic properties of the Fe cores. More generally, appropriate choice of shell material should allow the possibility to "engineer in" particular magnetic properties to the cores in magnetic core/shell clusters, either through structural change or lattice stretching. This will be important part of realising their use in potential applications, which include healthcare and information-and-technology related areas.

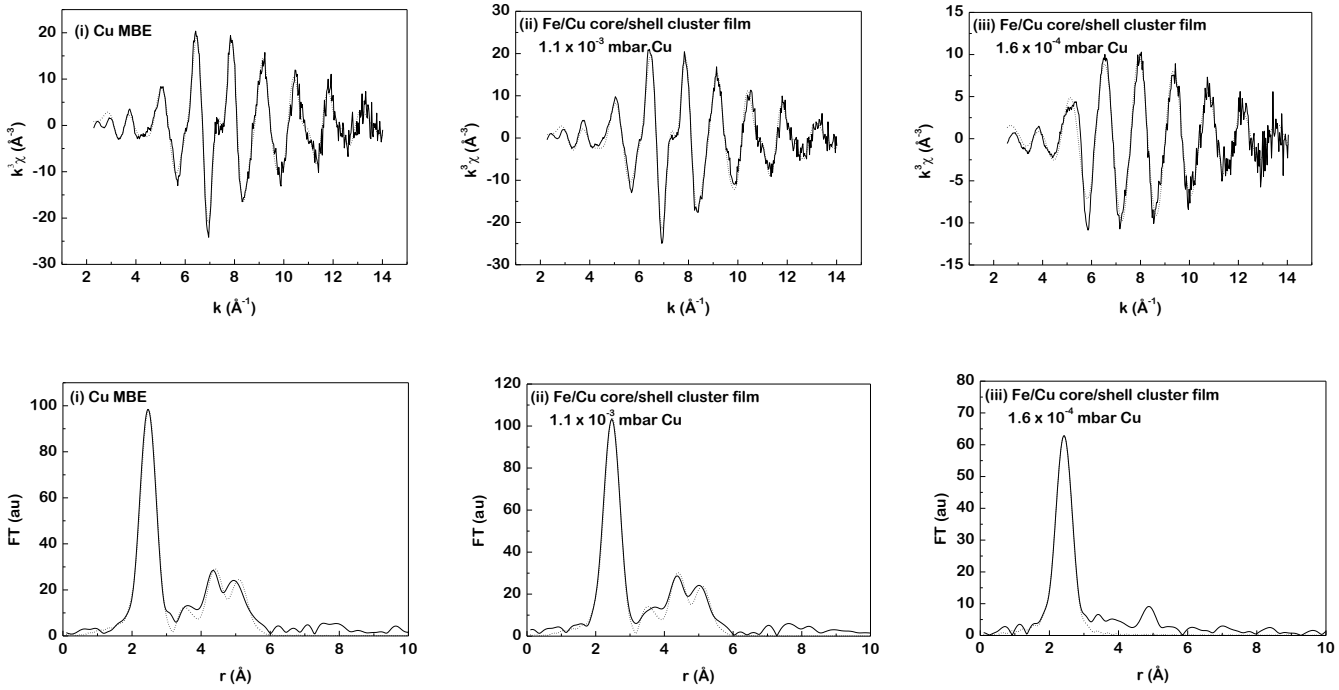

Figure 2 Cu K edge spectra for Fe/Cu films. Full lines – data; dashed lines – fit.

References

[1] S.H.Baker, M.Roy, S.Louch and C.Binns (2006) J.Phys.:CM **18** 2385

[2] S.H.Baker, A.M.Asaduzzaman, M.Roy, S.J.Gurman, C.Binns, J.A.Blackman and Y.Xie (2008) Phys.Rev. B **78** 014422

[3] S.H.Baker, S.C.Thornton, K.W.Edmonds, M.J.Maher, C.Norris and C.Binns (2000) Rev.Sci.Intsrum.**71** 3178