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Loss of long-range magnetic order in a nanoparticle assembly due to random anisotropy

C Binns[1], P B Howes[1], S H Baker[1], H Marchetto[2], A Potenza[2], P Steadman[2], S S Dhesi[1,2], M Roy[1], M J Everard[1] and A Rushforth[3]

[1] Department of Physics and Astronomy, University of Leicester, Leicester LE1 7RH, UK
[2] Diamond Light Source Ltd, Harwell Science and Innovation Campus, Diamond House, Chilton, Didcot, Oxfordshire OX11 0DE, UK
[3] School of Physics and Astronomy, University of Nottingham, Nottingham NG7 2RD, UK

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Abstract

We have used soft x-ray photoemission electron microscopy (XPEEM) combined with x-ray magnetic circular dichroism (XMCD) and DC SQUID (superconducting quantum interference device) magnetometry to probe the magnetic ground state in Fe thin films produced by depositing size-selected gas-phase Fe nanoparticles with a diameter of 1.7 nm (∼200 atoms) onto Si substrates. The depositions were carried out in ultrahigh vacuum conditions and thicknesses of the deposited film in the range 5–50 nm were studied. The magnetometry data are consistent with the film forming a correlated super-spin glass with a magnetic correlation length ∼5 nm. The XPEEM magnetic maps from the cluster-assembled films were compared to those for a conventional thin Fe film with a thickness of 20 nm produced by a molecular beam epitaxy (MBE) source. Whereas a normal magnetic domain structure is observed in the conventional MBE thin film, no domain structure could be observed in any of the nanoparticle films down to the resolution limit of the XMCD based XPEEM (100 nm) confirming the ground state indicated by the magnetometry measurements. This observation is consistent with the theoretical prediction that an arbitrarily weak random anisotropy field will destroy long-range magnetic order.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Thin films produced by depositing pre-formed size-selected gas-phase nanoparticles are an important class of materials, whose properties can be controlled by a number of parameters including the deposited particle size [1–3] and the landing energy [4]. In addition co-deposition of the particles and an atomic vapour, to produce a granular material of clusters embedded in a matrix, gives an extra degree of control through the volume fraction of the particles [5]. It has also been demonstrated that the choice of the matrix material allows one to modify the atomic structure of the embedded particles [6]. This high degree of control is especially important in magnetic materials and it has been shown that films of Co nanoparticles embedded in Fe matrices can have a saturation magnetization that exceeds the Slater–Pauling limit [2].

It is known that dense interacting assemblies of deposited nanoparticles are magnetically soft unlike the isolated particles [7] but the precise nature of the magnetic ground state in such films remains an open question. It is clear from low temperature magnetometry studies of Fe and Co nanoparticles embedded in Ag that the isolated nanoparticles have a uniaxial anisotropy and that the anisotropy axis of the deposited particles is randomly oriented in three dimensions [7]. Xie and Blackman have shown that all free Co clusters except those with magic numbers of atoms have a uniaxial anisotropy [8] and since the free clusters are rotating about all three axes, their anisotropy axis will be pointing in a random direction

at the point of impact. In a strongly interacting pure cluster assembly the exchange interaction will tend to produce magnetic alignment between clusters but the local magnetic anisotropy axis will change randomly in direction with a length scale of one nanoparticle (∼2 nm in our case).

Thirty years ago Imry and Ma [9] used both real-space domain and k-space fluctuation arguments to show that a random field, no matter how weak, would destroy long-range order in a system that was ordered in the absence of the random perturbation. This was only true for systems with four or less (extended) spatial dimensions, which is the case here. Later, Chudnovsky and co-workers [10–14] used a similar formalism to carry out a detailed study of the case where the random field is a random anisotropy applied to a ferromagnetic system, in which the anisotropy changes on a length scale much smaller than the domain width.

In their approach the magnetic ground state in a granular film is determined by the relative strength of a random anisotropy field.

$$H_r = \frac{2K_r}{M_s} \tag{1}$$

and an exchange field:

$$H_{ex} = \frac{2A}{M_s R_a^2}. \tag{2}$$

Here, K_r is the (randomly oriented) anisotropy of the grains, M_s is their saturation magnetization, A is the exchange constant for the interaction between the grains and R_a is the nanometre-scale region over which the local anisotropy axis is correlated, i.e. the characteristic grain size. The relative strength of the fields is given by the dimensionless parameter:

$$\lambda_r = \frac{H_r}{H_{ex}}. \tag{3}$$

The RA model predicts that the approach to saturation of the magnetization of the films in an applied field H is given by:

$$M = M_s\left(1 - \frac{1}{30}\frac{\lambda_r^2}{\sqrt{h_{ex}}}\int_0^\infty \mathrm{d}x\, C(x)x^2 \exp\left[x\sqrt{h_{ex}}\right]\right), \tag{4}$$

where $h_{ex} = H/H_{ex}$, and $C(x)$ is the correlation function for the anisotropy axes with x in units of R_a. In a cluster-assembled film with monodisperse clusters, $C(x)$ can be taken to be a simple step function with a cut-off at $x = 1$. A key feature of the RA model is that it describes how pure cluster films can be magnetically soft when composed of clusters with a high anisotropy constant by an averaging of the anisotropy to close to zero.

The model was originally applied to amorphous films in which a local, randomly oriented, anisotropy is due to local atomic disorder. It is even better suited to describing the magnetization in films of deposited nanoparticles in which the distance R_a over which an anisotropy axis is correlated is well defined (i.e. the particle diameter). For $\lambda_r > 1$ the magnetic correlation length at zero field is R_a, and the magnetic vector in each particle points along the local intra-particle anisotropy axis. With increasing inter-particle exchange (or decreasing intra-particle anisotropy) the configuration becomes a correlated spin glass (CSG) in which the magnetization vector in neighbouring particles is nearly aligned but the random deviation of the moments from perfect alignment produces a smooth rotation of the magnetization throughout the system with a magnetic correlation length that is a factor $1/\lambda_r^2$, larger than the particle diameter. Since we are talking about the alignment between the super-moments of single-domain particles it is more appropriate to call this state a correlated super-spin glass (CSSG). Thus at $\lambda_r = 1$ the ground state changes from a simple spin glass where the magnetization in each nanoparticle points in a random direction to a CSSG and the difference between the two configurations is illustrated in figure 1. The RA model has been used successfully to model the magnetization data in several *ex situ* magnetometry studies of deposited nanoparticle films [5, 7, 15–18].

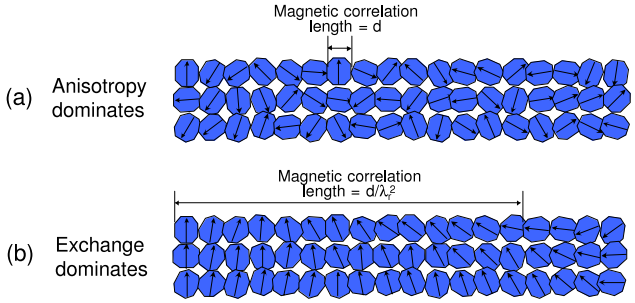

Figure 1. A stack of randomly oriented nanoparticles with the slight elongation of each one representing the anisotropy axis. In (a) $\lambda_r \geqslant 1$ and the magnetization vector points along the local anisotropy axis so the magnetic correlation length is a single particle diameter (simple spin glass). In (b) $\lambda_r < 1$ and the magnetic vectors are nearly aligned. The random perturbation from perfect alignment results in a finite magnetic correlation length that is a factor $1/\lambda_r^2$ larger than a single particle (correlated super-spin glass).

A simpler intuitive argument for the loss of long-range order emerges from a consideration of the average displacement from perfect alignment between two neighbouring nanoparticle moments. If the magnetization vector of a particle is taken as a reference axis relative to which the anisotropy axis of a neighbouring particle makes an angle ϕ, then if the angle between the magnetization vectors of the two particles is θ the value of θ will be given by the minimum of the energy term:

$$H_{ex}\langle\cos\theta\rangle + H_r\langle\sin^2(\phi - \theta)\rangle. \tag{5}$$

Along a line of N particles the value of N required for the average displacements to add up to 90° (when correlation with the original spin is lost) is proportional to $(H_{ex}/H_r)^2$, that is, proportional to $1/\lambda_r^2$, as predicted by the RA model.

The conclusion of this simple argument or the full-blown RA model is that in the absence of an applied field, a film of deposited nanoparticles should exhibit no domain structure. The uniformly rotating magnetization of the CSSG state produces no external field and thus removes the competition between the magnetostatic term and the exchange interaction, which in a normal film produces domains. Magnetization patterns above a deposited nanoparticle film have been obtained using magnetic force microscopy (MFM) and show a randomized patchwork of fields at the nanoscale as expected

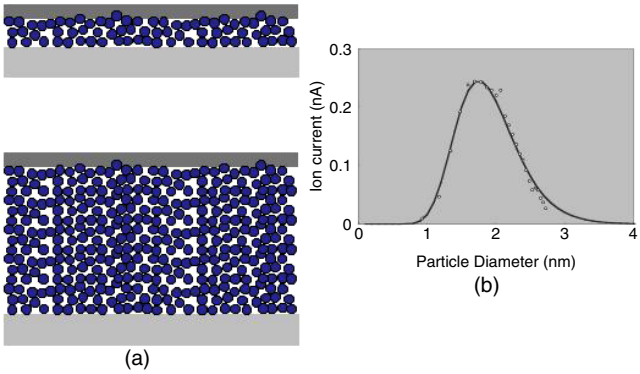

Figure 2. (a) Schematic of the samples studied, consisting of different thicknesses of Fe nanoparticles deposited in UHV onto Si substrates with a 2 nm thick carbon cap to prevent oxidation on transfer through air to the XPEEM. (b) Size distribution of the gas-phase nanoparticles fitted to a log-normal curve, giving a most probable diameter of 1.7 nm with a standard deviation of 0.24.

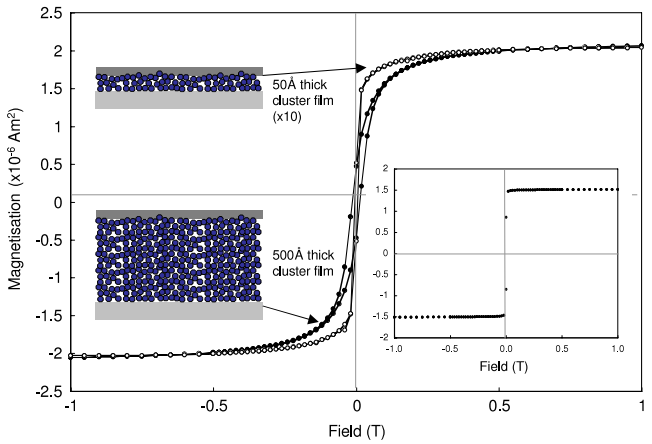

Figure 3. In-plane magnetization curves at 298 K from cluster films 50 Å thick and 500 Å grown on Si(100). The inset shows the magnetization curve from a 200 Å thick film grown by MBE deposition.

for a CSSG [19, 20]. In all cases studied so far however the films were composed of core–shell Co/CoO particles and in addition the stray field from an MFM tip can be more than 1000 Oe [21] depending on the imaging conditions and the tip coating and thus be strong enough to alter the magnetization pattern of the ground state [11].

Here we present a study carried out using x-ray photoelectron microscopy (XPEEM) and DC SQUID magnetometry of Fe nanoparticles deposited in UHV conditions and capped with ultra-thin carbon films for transfer through air. We verified the sample cleanliness *in situ* by observing the lineshape of the L-absorption edge and the XPEEM images were obtained in fields of less than 10 G thus the complications associated with the previous MFM studies are removed.

2. Experimental details

The Fe nanoparticle films were produced using an ultra-high vacuum (UHV) compatible gas aggregation source described elsewhere [22]. Aerodynamic lensing within the high-pressure section of the source is used to boost the flux and narrow the size distribution, which is measured in the gas-phase using a quadrupole mass spectrometer operating up to a mass of 350 000 Daltons. The measured size spectrum shown in figure 2(b) has been fitted to a log-normal distribution and it is observed to peak at a diameter of 1.7 nm with a standard deviation of 0.24. The clusters were deposited onto polished Si(100) substrates and the equivalent thickness was determined using a quartz oscillator. Each film was coated with a 2 nm carbon cap deposited using an electron beam evaporator to protect the films from oxidation.

The samples were installed in the UHV end-station of beamline I06 on the DIAMOND synchrotron, UK. The beamline source is a pair of Apple II undulators working in the soft x-ray regime that can produce left and right circularly polarized x-rays. A plane grating monochromator provides a resolving power of up to 10 000 and a pair of Kirkpatrick–Baez mirrors focus the x-ray light to illuminate a 10 μm diameter spot on the sample. Photoelectrons are collected by an Elmitec [23] photoelectron emission microscope (PEEM) for two polarisations states of the incident light, which can provide a magnetic contrast image of the emitted photoelectrons with a spatial resolution of ∼100 nm. Magnetic contrast is obtained by comparing images obtained using x-rays at the Fe $L_{2,3}$ edges with those obtained off the absorption edge. XMCD therefore provides a contrast for magnetic domains parallel and antiparallel to the x-ray polarization vector for a correctly aligned sample.

Magnetization curves from the films were obtained using a Quantum Design MPMS XL1 SQUID magnetometer in the School of Physics and Astronomy at the University of Nottingham. The diamagnetic response of the substrate has been subtracted from the data presented in this paper.

3. Results

DC SQUID magnetization measurements of the cluster films with thicknesses 50 and 500 Å taken at 298 K are shown in figure 3. The qualitative shape of the curves is similar to previous magnetometry measurements of cluster-assembled films [5, 7] and the small hysteresis ($H_c = 0.005$ T and $H_c = 0.014$ T for the 50 Å and 500 Å films respectively) is ascribed to a coherent anisotropy in the film. For comparison the inset shows a magnetization curve from a 200 Å thick Fe film grown by MBE deposition on Si(100) in the same deposition chamber and displays the abrupt switching behaviour expected for a thin film magnetized in-plane. The rounded approach to saturation in the cluster films should follow the curve predicted by equation (4) and fits to the data are shown in figure 4. In both cases a value of λ_r of 1 was used, i.e. at the crossover between the simple and the correlated spin glass with the value of the exchange field in the thinner film being about half of that in the thick film. It is possible to get reasonable fits with λ_r less than 1 but below about 0.7 it becomes impossible to fit the data (see section 4). Thus we can state that the magnetic correlation length is only about 1 or two clusters (∼5 nm). This

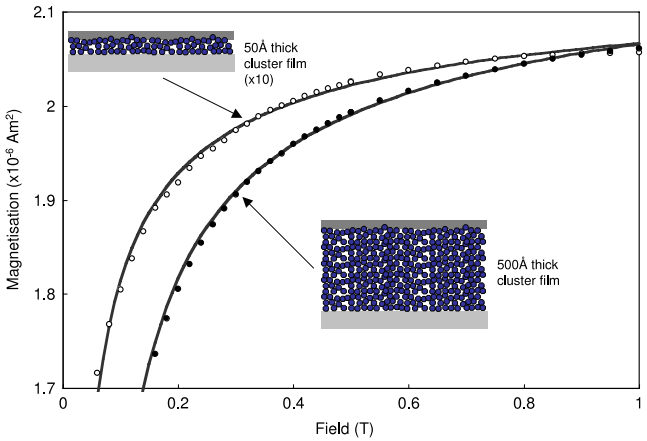

Figure 4. Fits using equation (4) (lines) to model the measured approach to saturation (circles) of the 50 and 500 Å thick cluster films. In both cases it is only possible to get fits with reasonable values for the exchange and anisotropy fields if values of λ_r close to 1 are used.

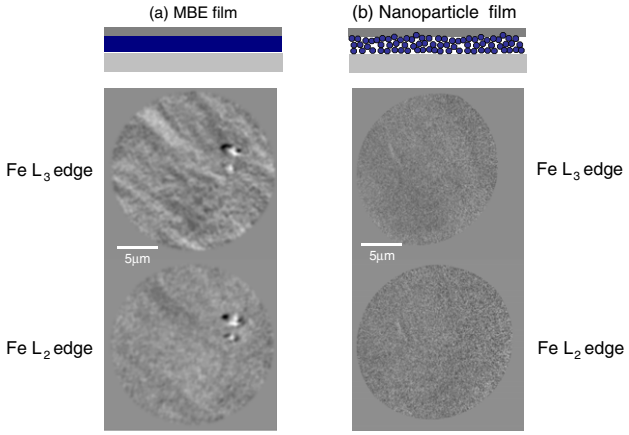

Figure 5. (a) XPEEM images at the Fe L_3 and L_2 edges of the domain structure in a 200 Å thick MBE-grown film on Si(111). (b) Similar XPEEM image from the cluster-assembled film showing no sign of a domain structure. The lack of domain structure was observed at all angles and for both (thick and thin) cluster-assembled films and is ascribed to the very short correlation length (∼5 nm) of the CSSG state as predicted from the magnetometry data.

is well below the resolution limit of the XPEEM (∼100 nm) so from the magnetometry data we would predict that the XPEEM images from cluster-assembled films should show no evidence for a domain structure.

The two samples most studied using XPEEM were the 200 Å thick MBE-grown film and the 500 Å thick nanoparticle film. The x-ray absorption across the Fe edge showed the same L_3-edge peak jump relative to the background in both films, which is to be expected despite the different thicknesses since the film thickness exceeds the photoelectron escape depth in both cases. Figure 5(a) shows the XPEEM images from the Fe L_3 and L_2 edges of the 200 Å thick MBE-grown film and a typical domain pattern for a thin film is observed with opposite contrast at the two edges as required. The data shows specifically the ratio of absorption strengths for the two opposite helicities of the beam after correcting for the detector response. To obtain these images the sample was rotated to optimize the contrast and we also checked that rotating the sample by 180° negated the image. The relatively weak contrast is partly due to the 2 nm thick carbon layer deposited in order to protect the magnetic films from oxidation. Thus there is a significant background photoelectron signal from the non-magnetic cap. The change in dichroism between domains is ∼6%, that is, significantly weaker than the maximum value of ∼40% expected for antiparallel domains in a perfectly aligned sample. We ascribe this to neighbouring domains oriented at less than 180° to each other, which is not unexpected in a polycrystalline film. In addition the image contrast is affected by the alignment of the PEEM and the precise imaging conditions. We rule out a weak dichroism as a result of oxidation of the film since the L-edge XAS lineshape was characteristic of clean Fe. The step edges at the domain boundaries gives a measured resolution of ∼100 nm.

Figure 5(b) shows similar XPEEM images at the two edges from the 500 Å thick cluster-assembled film. Uniform grey images such as this were observed at all sample rotation angles. In addition there was no overall intensity variation with angle demonstrating that the sample was not uniformly magnetized in agreement with the magnetometry data, which shows that the remanence is very small. It is clear that, even with the relatively low contrast observed in the MBE-grown film, a domain structure should be observed in the nanoparticle film if it was there. This lack of domain structure was observed on both cluster-assembled films demonstrating that the intrinsic mesoscopic magnetic ordering in the nanoparticle films is on a scale less than the resolution limit of the XPEEM using XMCD contrast, that is, ∼100 nm.

4. Discussion

The XPEEM images show no evidence for a domain structure larger than 100 nm and for films of this thickness the domain wall width is expected to be ∼50 nm [24]. The observation demonstrates that the magnetic ground state of the nanoparticle films cannot be differently oriented domains separated by domain walls so they display no long-range order. This can be ascribed to the random anisotropy field produced by randomly oriented 2 nm grains. It is useful to try and be more specific about the ground state, for example to distinguish between a simple (super)-spin glass and a correlated super-spin glass. From the point of view of the random anisotropy (RA) model, there is not a sharp distinction, that is, the simple spin glass is the high-intra-cluster-anisotropy (low inter-cluster-exchange) extreme. These parameters are characterized by the random anisotropy and exchange fields, H_r and H_{ex} respectively, defined in equations (1) and (2). Their ratio (H_r/H_{ex}) denoted by λ_r (equation (3)) determines the magnetic correlation length by $1/\lambda_r^2$. The correlation length varies continuously, decreasing as the intra-particle anisotropy increases and reaches the size of a single particle when $\lambda_r = 1$ at which point the ground state is a simple (super)-spin glass. It is not possible to get an accurate value of λ_r from the magnetometry data (figure 4) since by choosing different

values of H_{ex} or H_r one can optimize the fits for different values of their ratio and the global minimum is too shallow to be found given the noise and a small intrinsic uncertainly about the linear background magnetization due to the substrate. In practise however it is impossible to get good fits for $\lambda_r < \sim 0.7$, giving a correlation length of only two clusters or ∼5 nm. The ground state of the nanoparticle films is thus close to the simple super-spin glass limit of the CSSG.

Another possible ground state is a re-entrant spin glass, which includes some degree of long-range order [25] without a distinguishable domain structure. We can't rule this out but the agreement between the magnetometry data and the RA model leads us to ascribe the loss of long range order to the frustration between the random anisotropy and exchange interactions induced by the nanostructuring of the sample.

5. Conclusion

XPEEM combined with XMCD has shown that films assembled from pre-formed nanoparticles with a diameter of 1.7 nm (∼200 atoms) on Si substrates do not form a magnetic domain structure. Furthermore, DC SQUID magnetometry implies that the nanoparticle films form a correlated super-spin glass with a magnetic correlation length <5 nm. This is consistent with the prediction by Imry and Ma [9] that a random field, no matter how weak, will destroy long-range order in a system that is ordered in the absence of the random perturbation. In the present case, the random field is a random anisotropy field produced by the arbitrary direction of the magnetic anisotropy of each nanoparticle. This type of magnetic system was specifically dealt with by Chudnovsky and co-workers [10–14] and here we have shown that thin films composed of nanoparticles do indeed form a correlated super-spin glass (CSSG).

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