

Exchange Bias in Fe@Cr Core-Shell Nanoparticles

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Abstract

We have used X-Ray Magnetic Circular Dichroism (XMCD) and magnetometry to study isolated Fe@Cr core-shell nanoparticles with an Fe core diameter of 2.7 nm (850 atoms) and a Cr shell thickness varying between 1 and 2 monolayers. The addition of Cr shells significantly reduces the spin moment but does not change the orbital moment. At least two Cr atomic layers are required to stabilize a ferromagnetic/antiferromagnetic interface and generate the associated exchange bias and increase in coercivity.

Main Text of Communication

Gas-phase synthesis of nanoparticles offers the new capability to engineer nanoparticles at the atomic level and then use them to produce novel materials by depositing them onto surfaces, either alone or in conjunction with a molecular beam of a matrix material^[1-3]. In particular recent developments have enabled the synthesis of alloy^[4] and core-shell^[5,6] nanoparticle building blocks in which there is independent control over core size, shell thickness and flexible choice of element in either. In the work reported here we have exploited this flexibility to study how the magnetic behaviour of Fe nanoparticles evolves as they are coated with one or two monolayers of Cr. The motivation for doing this is to understand the nature of the magnetic interface as a function of Cr shell thickness and to search for the onset of the Exchange Bias phenomenon.

Exchange Bias (EB) is the term used to describe unidirectional anisotropy, or the horizontal shift in the magnetisation loop in systems containing a ferromagnetic(F)/antiferromagnetic(AF) interface when they are field-cooled below the Néel temperature of the AF material. It was first observed over 50 years ago in 20 nm diameter Co nanoparticles, partially oxidized to form an AF CoO shell^[7]. The original explanation was given in terms of a flat F/AF interface with a layered antiferromagnet whose spins are pinned in a single direction by the rest of the AF material at the interface. Rotating the F material by an external field produces a shift in the magnetic loop given by the difference in exchange between parallel and antiparallel spin alignments at the interface. The

problems with this proposal are that the observed loop shifts are much smaller than would be given by the exchange interaction along the entire interface and the effect is observed in systems where the AF material is not a layered antiferromagnet and the interface is not flat (as in the original discovery). Nevertheless after decades of research (for reviews see ^[8,9]) the general conclusion is that EB does arise from pinned magnetic moments in the AF material at the interface though in a typical system, only a small proportion of the spins are pinned^[10].

The vast majority of research has been conducted on flat interfaces in thin films (for reviews see^[11,12]), largely driven by the important applications of these systems in spin valves used in read heads in magnetic recording^[13]. Despite the original observation of EB in nanoparticles, there have been relatively few studies of nanoparticle systems containing a F/AF interface and so are less well understood. However these systems are becoming increasingly important in nanotechnology, which has led to a reemergence of interest in this field. The appearance of EB is accompanied by a large increase in anisotropy and coating F nanoparticles with an AF shell has often been proposed as a way of modifying the anisotropy^[14]. This would be important for future single nanoparticle data storage systems or optimizing the performance of magnetic nanoparticles in applications such as hyperthermia treatment of tumours^[15].

The majority of nanoparticle systems studied to date have been F particles in oxide AF matrices however the advent of cluster deposition has provided the opportunity to embed size-selected nanoparticles in metallic AF matrices. Systems studied so far include 1.8 nm diameter Co nanoparticles^[16,17] and 1.9 nm Fe nanoparticles^[18] embedded in Mn matrices. Both these systems show clear exchange bias and increased width magnetization loops despite a high degree of alloying in the Co/Mn case. More recently it was found that Fe nanoparticles embedded in Cr matrices, in which there is a well-defined interface, showed an extremely small EB at the lowest Fe nanoparticle volume fraction^[19,20].

Clearly more research is required to understand the F/AF interface within nanoparticles. Here we exploit the development of a new method of synthesis^[5] to produce well-defined Fe@Cr core-shell nanoparticles with an Fe core diameter of 2.7 nm and Cr shell with a thickness of either zero, one or two monolayers embedded at low volume fraction (3-4%) in non-magnetic Ag matrices. This affords the opportunity to study how the magnetism at the F/AF interface develops with increasing thickness of the AF shell. It has been known for some time that in Cr layers deposited onto flat Fe surfaces, the direction of surface magnetisation oscillates as a function of Cr layer thickness with a period of two monolayers^[21] and it is assumed that the magnetisation at the Fe surface is unaffected. Here we study the magnetic behaviour as the Cr layer grows around Fe nanoparticles, which is a highly frustrated system in which different behaviour is expected. It has been shown that the magnetic behaviour of the Fe/Cr interface is highly sensitive to the details of the topography^[22].

The synthesis method is sketched briefly in Fig. 1. An Ultra-High Vacuum (UHV) compatible thermal gas aggregation source described elsewhere^[23] produces the core Fe clusters and the shell is deposited onto the free gas-phase nanoparticles by passing them through a tubular heated crucible^[5] containing Cr. The Cr thickness can be varied simply by changing the crucible temperature. The core-shell nanoparticles are then deposited onto substrates in a UHV deposition chamber in conjunction with an atomic Ag vapour from a Knudsen cell so that they are matrix isolated in Ag. For the samples studied here the volume fraction of nanoparticles was 3 – 4%. The entire process of cluster production, shell evaporation and deposition with the matrix takes place with partial pressures of contaminant gases such as CO, H₂O, O₂ in the 10⁻¹¹ mbar regime although there is a background of ~10⁻⁶ mbar pure He from the cluster source. The samples were deposited onto Cu Transmission Electron Microscope (TEM) grids coated with a 100Å thick C film to a thickness calculated to give a 10% - 90% X-ray transmission around the Fe L_{2,3} edge thus enabling the direct measurement of soft X-ray absorption. The X-Ray Magnetic Circular Dichroism (XMCD)

measurements were carried out on beamline I06 of the Diamond Light Source, UK and subsequently the magnetometry was carried out on the same samples using a SQUID magnetometer.

Fig. 1(b) shows the mass spectrum of the core Fe nanoparticles measured in the gas-phase fitted to a log-normal distribution and compared to the size determined by fitting a Langevin function to the magnetization curve (see Fig. 2(d)) and the estimated size obtained from TEM images. The median of the log-normal distribution, the ‘magnetic’ size and the imaged size all agree to within a margin of ± 0.15 nm. For the remainder of this report we will assume the diameter of the core Fe nanoparticles to be as obtained from fitting the Langevin function, that is, 2.68 nm or ~ 850 atoms as this is the most reliable representation of the size that produces the observed magnetic behaviour.

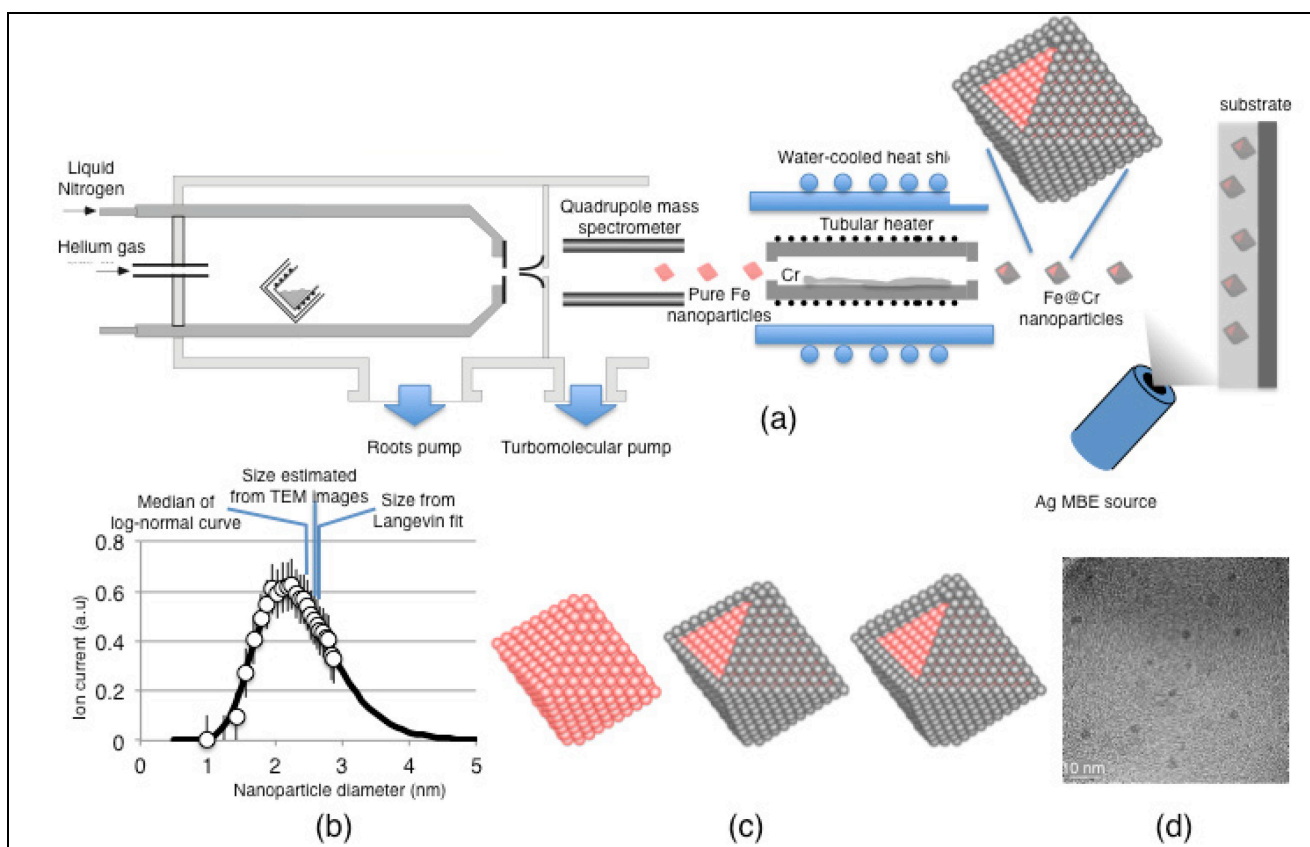


Fig. 1 (a) Synthesis of core-shell nanoparticles and production of matrix-isolated assemblies for XMCD and magnetometry studies. (b) Mass spectrum of pure Fe nanoparticles measured in the gas phase (open circles) fitted to a log-normal distribution (line). The spectrum is compared to the size determined by fitting Langevin functions to the magnetization curves and estimated from TEM images. All three methods agree on the core particle diameter within the experimental uncertainty. (c) Illustration of the three types of nanoparticle studied, i.e. pure Fe, Fe@Cr with a monolayer shell and Fe@Cr with a bilayer shell. (d) TEM image showing size distribution of Fe@Cr bilayer nanoparticles.

Two different thicknesses of Cr shell were deposited on the core Fe nanoparticles and characterised by comparing the integrals over the Cr $L_{2,3}$ and Fe $L_{2,3}$ absorption edges, yielding 280 atoms and 750 atoms or nominally a monolayer and bilayer of Cr. The three different types of nanoparticle in the samples are illustrated in Fig. 1(c). High-resolution TEM images of the Fe@Cr nanoparticles did not unambiguously reveal the atomic structure however recent EXAFS measurements of Fe nanoparticles of the same size co-deposited with Cr matrices^[19,20] showed that the Fe nanoparticles, in common with the Cr matrix, have a bcc structure. The EXAFS data also showed that the interface is sharp with little alloying and there is an excellent epitaxial match between the Fe and Cr bcc and the Ag fcc crystal lattices. It is thus reasonable to assume that the structure of the Fe@Cr nanoparticles in the Ag matrix is close to the ideal illustrated in Fig. 1(c).

Fig. 2(a) shows the raw soft X-ray absorption data from the sample containing pure Fe nanoparticles taken with negative (nc) and positive (pc) X-ray circular polarization through the Fe $L_{2,3}$ edge normalized to the beam intensity for an applied field of -6T and sample temperature of 204K. The data after subtracting a linear pre-edge background and an integral background fitted under the absorption peaks is plotted in Fig. 2(b). Removal of the integral background reveals the weak Ag M_1 edge at around 730 eV. This vanishes when the two spectra are subtracted (Fig. 2(c)) so the dichroism spectra can be integrated accurately to apply the sum rules though the Ag peak introduces an additional error of $\pm 5\%$ due to the uncertainty in the total Fe $L_{2,3}$ edge intensity.

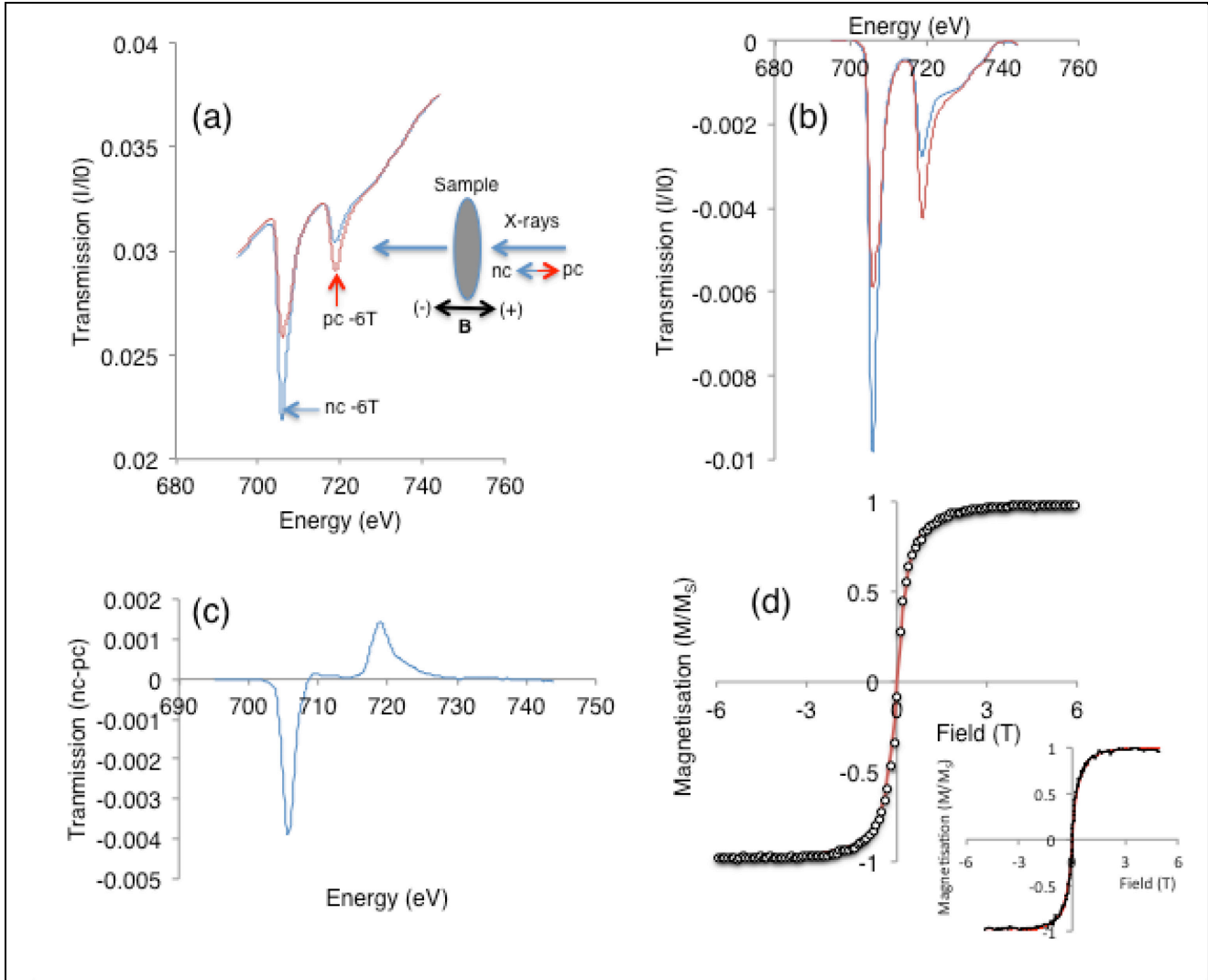


Fig. 2 (a) X-ray transmission in the Fe $L_{2,3}$ region of pure Fe nanoparticles in Ag with an applied field of -6T showing the difference in absorption between negative circular polarization (nc) and positive circular polarization (pc) of the X-rays. The inset shows the labelling of positive and negative directions of the applied field and photon angular momentum. (b) Absorption data after subtracting an integral background. (c) Fe $L_{2,3}$ dichroism used for sum rule analysis. (d) Sample magnetization at 204 K (open circles) obtained by plotting the intensity of the Fe L_3 peak as a function of the applied field. The red line is a Langevin function plotted for a particle diameter of 2.68 nm. The inset compares the magnetization measured by XMCD (black line) with that measured from the same sample by SQUID magnetometry (red line) showing excellent agreement.

The dichroism data was analysed using the magneto-optical sum rules to obtain the orbital, spin and total magnetic moments per atom^[24]. Averages were obtained over the combinations of field and X-ray polarisations: -6T nc-pc, +6T nc-pc, ± 6 T nc, ± 6 T pc and the values obtained are listed in table 1 for sample temperatures of 2K and 204K. In all calculations it was assumed that there are 3.39 holes per atom as used in previous analysis of XMCD data from Fe thin films^[24]. All the absorption spectra were measured at normal incidence and as shown in previous work^[25], for Fe nanoparticles of this size, the dipole moment contribution reduces the measured spin moment by $\sim 0.1 \mu_B$ so the

total saturation moment at 2 K, including the dipole correction, is closer to $2.28 \mu_B$. This is the value to be compared to that obtained by magnetometry and is, within the error, in agreement with the accepted bulk value of $2.22 \mu_B/\text{atom}$, though it appears that there is a slightly enhanced orbital moment relative to the bulk value ($0.085 \mu_B/\text{atom}$ ^[24]). By comparison, the orbital moment measured from exposed Fe nanoparticles of a similar size on graphite surfaces in UHV is $\sim 0.2 \mu_B/\text{atom}$ ^[25].

Table 1 Spin, orbital and total magnetic moment per atom for pure Fe and Fe@Cr nanoparticles in Ag

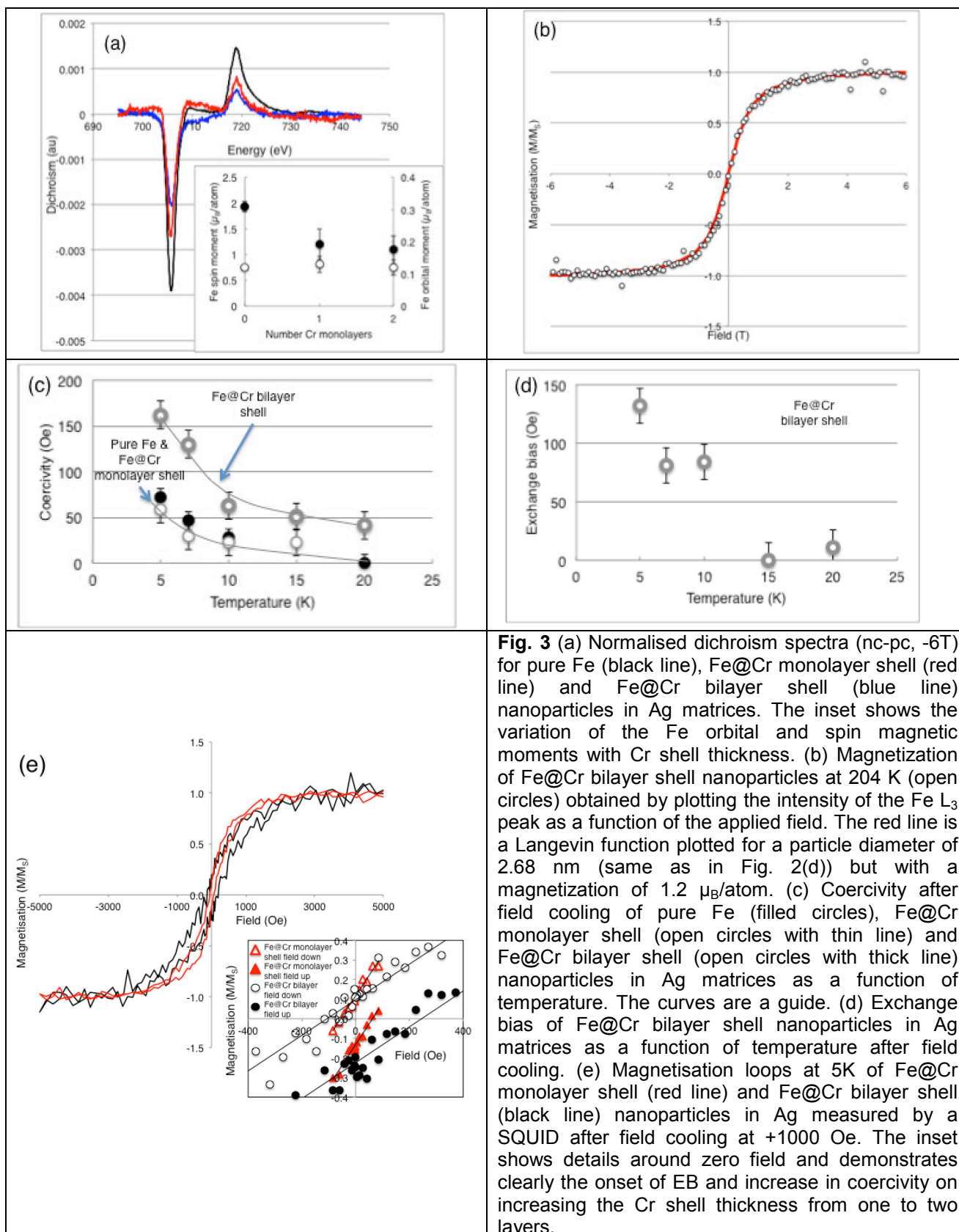
Sample	Temperature (K)	Orbital moment/atom (μ_B)	Spin moment/atom (μ_B) (no dipole correction)	Total moment/atom (μ_B) (without dipole correction)
Pure Fe	2	0.11 ± 0.02	2.07 ± 0.16	2.18 ± 0.16
Pure Fe	204	0.12 ± 0.02	1.83 ± 0.11	1.95 ± 0.11
Fe@Cr monolayer	204	0.13 ± 0.03	1.2 ± 0.3	1.3 ± 0.3
Fe@Cr bilayer	204	0.12 ± 0.03	1.1 ± 0.3	1.2 ± 0.3

The magnetization vs. field obtained at 204 K by measuring the intensity of the Fe L_3 absorption peak as a function of applied field is shown in Fig. 2(d) (open circles) and compared to a Langevin function assuming a saturation magnetization of $2.28 \mu_B/\text{atom}$ (line). The fit to the data is optimized for a particle diameter of 2.68 nm (850 atoms). The inset in Fig. 2(d) shows a comparison between the magnetization curve measured by XMCD and that from the same sample at 200K measured by a SQUID magnetometer and demonstrates the excellent agreement between the 2 methods.

Fig. 3(a) shows a comparison of the Fe $L_{2,3}$ dichroism at 204K of pure Fe nanoparticles (black line), Fe@Cr monolayer shell (red line) and Fe@Cr bilayer shell (blue line) nanoparticles in Ag. The spectra have been normalized to the edge jump measured for each sample and it is immediately apparent that the dichroism is much weaker in the core-shell particles. The signal to noise in the data for the Cr coated nanoparticles is lower as these films were thinner and therefore contained less Fe than the pure Fe nanoparticle samples. However values for the Fe orbital and spin moments can still be obtained with an estimated error of $\pm 25\%$ and are listed in Table 1 and plotted in the inset in Fig. 3(a). The error is mainly due to the uncertainty in the background caused by the presence of the Ag M_1 feature. Despite the relatively large error it is apparent that the presence of either a monolayer or bilayer Cr shell reduces the Fe spin moment to around $1.1 - 1.2 \mu_B/\text{atom}$, while the orbital moment is not significantly affected. Approximately 40% of the Fe atoms in the core Fe nanoparticle are at the interface atomic layer so the lowering of the spin moment by 40% ($1.83 - 1.1 \mu_B/\text{atom}$) implies that the entire Fe surface layer is not ferromagnetic. This could be due either to a disordered or an AF Fe spin configuration at the interface but as we show below a F/AF interface develops in the case of the Cr bilayer shell and we ascribe the arrangement to be disordered in the case of the monolayer shell. The reduction in spin moment also highlights the difference between flat and nanoparticle interfaces as no reduction in Fe spin moment has been observed in epitaxial Fe/Cr multilayers^[26]. A significant reduction in the Fe moment has been observed in an epitaxial Fe/Cr interface after roughening by Ar sputtering^[22].

Independent confirmation of the total moment in the case of the Fe@Cr bilayer nanoparticles was obtained by fitting a Langevin function to the magnetization curve obtained by plotting the intensity of the Fe L_3 absorption peak as a function of applied field (Fig. 3(b)). In the fit it was assumed that the core Fe size remains at 850 atoms and the saturation magnetization was adjusted to optimize the fit. This occurs for a moment of $1.2 \mu_B/\text{atom}$, which agrees within the error with the XMCD value ($1.1 \pm 0.3 \mu_B/\text{atom}$) for this sample. The total moment is also in agreement with the value obtained by magnetometry for pure Fe nanoparticles embedded at low volume fraction in Cr matrices^[19,20].

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SQUID magnetometry was carried out on the same samples as used for the XMCD measurements and the measured coercivity as a function of temperature after field cooling in an applied field of +1000 Oe is shown in Fig. 3(c). For the pure Fe nanoparticles the decay can be understood simply by the transition from a blocked to a superparamagnetic state. For a given particle volume, V the blocking temperature, T_B , assuming a uniaxial anisotropy is given by:

$$T_B = \frac{KV}{k_B \log_e \left(\frac{\tau_m}{\tau_0} \right)}$$

where K is the particle anisotropy energy density, τ_{\square} is the characteristic time of the experiment and τ_0 is the lifetime of the nanoparticle magnetic moment at the high temperature limit. Previous measurements for Fe nanoparticles of a similar size embedded in Ag have provided values for K of $2.4 \times 10^5 \text{ Jm}^{-3}$ ^[27] and for τ_0 of 10^{-8} s ^[28]. The value of T_B is not very sensitive to τ and normally 100 s is chosen for a magnetization sweep in magnetometry, giving, for a particle size of 2.68 nm, $T_B = 7.6 \text{ K}$. The coercivity is clearly decaying at 7.6 K but doesn't vanish till about 20K due to the size distribution of Fe nanoparticles. This implies that the largest particles in the assembly have a diameter of about 3.7 nm, which agrees with the size distribution plotted in Fig. 1(b).

It is observed that Fe@Cr monolayer shell nanoparticles show a similar behaviour indicating that their decay in coercivity with temperature is also due to a blocked to superparamagnetic transition. Neither the pure Fe or the Fe@Cr monolayer shell nanoparticles showed any evidence for exchange bias after field cooling in an applied field of 6T. Note that in the case of the pure Fe nanoparticles this shows that the embedded particles are clean as a surface oxide produces an exchange bias. On the other hand, after field cooling the samples containing Fe@Cr bilayer shell nanoparticles an exchange bias appeared and its temperature dependence is plotted in Fig. 3(d). It is also observed that the coercivity in this sample is enhanced (Fig. 3(c)). Finally, Fig. 3(e) shows magnetisation sweeps for the Fe@Cr monolayer shell and Fe@Cr bilayer shell samples showing directly the onset of EB and increase in coercivity in going from a monolayer to a bilayer shell.

Both of these effects are associated with a F/AF interface and the conclusion is clear, that is, the F/AF interface requires at least two Cr monolayers around the Fe cores to develop. It is evident from the temperature decay of the exchange bias and the coercivity that the Néel temperature of the Cr in the Fe@Cr bilayer shell nanoparticles is much less than the Cr bulk value of 308 K.

We propose the following description of how the interface develops. Adding a single monolayer of Cr produces an Fe surface with disordered spins and from the reduction observed (~40%) the entire Fe surface layer of each nanoparticle contributes zero net moment to the total magnetisation. Within this structure there are no pinned moments that would produce EB. It is possible that there is some intermixing of Fe and Cr but there is no direct evidence for this. Adding the second Cr layer stabilises an AF shell, which extends into the surface of the Fe nanoparticles, thus each surface Fe atomic layer still contributes zero net moment and the measured moments remain the same as in the Cr monolayer case. Surface AF configurations in Fe have also been proposed in the case of stepped Fe/Cr interfaces^[29]. In reality there is likely to be a good deal of disorder in the bilayer case also as the number of spins that are required to be pinned to produce the observed EB is rather small. It was demonstrated by Ohldag et al^[10] in the case of Co/MnIr interfaces that only ~4% of atoms at the interface were pinned to produce an EB of 600 Oe, compared with 150 Oe in our system. Although the details of the interface and thus the interface energy per unit area are different we can conclude that only a few interface atoms need to be pinned to generate the observed EB in Fe@Cr bilayer nanoparticles.

These results are important for the future development of complex core-shell nanoparticles for applications. Having ferromagnetic/antiferromagnetic combinations of elements is often suggested as a way of controlling the anisotropy but the high degree of frustration produced by having a nanoscale spherical interface as opposed to a flat one has a profound effect on the magnetic behaviour.

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