Superparamagnetism in Heterogeneous AgFe Thin Films – A Low Energy μ SR Study

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Abstract. This paper describes a study of superparamagnetism in iron nanoclusters using low energy μ SR, including for the first time zero field measurements, which yield an intrinsic nanocluster superparamagnetic relaxation rate of $\nu_0 = 67 \pm 15$ MHz and an energy barrier of $\Delta E = 37 \pm 4$ K. TEM micrographs of the embedded clusters show there to be a range of shapes and also sizes, which is borne out by SQUID magnetometry measurements.

1. Introduction

We have previously shown the utility of the transverse field low energy μ SR method for studies of superparamagnetism in iron nanoclusters prepared in a thin film. Such a sample is too thin for study with conventional muon techniques. An energy barrier of $\Delta E = 51 \pm 9$ K, activation rate ν_0 of the order of 10^8 Hz were determined, and an anisotropy constant of $K_c = 0.23 \pm 0.04$ MJ m⁻³ with the assumption of cubic anisotropy [1]. In this work we have extended our experiments to include zero-field low energy μ SR, a technique different from the transverse field measurements reported previously. We present the first transmission electron microscope images of our iron nanoclusters, which along with SQUID magnetometry allows us to estimate the real shape and size of the clusters. These non-nuclear methods of investigation are given equal weight with μ SR in our paper, for they are crucial to providing a physical interpretation of the μ SR data.

The sample for μ SR measurements was a thin film prepared in a gas condensation source similar to that described previously [2]. A silver substrate was used. A 30 nm thick silver buffer was deposited before the 147 nm thick silver layer containing the iron nanoclusters at a concentration of order 0.1% at the

centre of the deposition flux. The buffer layer ensures that the nanocluster layer is homogeneous in composition and microstructure irrespective of the substrate surface. The nanoclusters are formed separately in the source from the flux of silver so can not be considered to be embedded in silver before they land on the substrate. Finally, a 10 nm silver capping layer was deposited. The cap is a barrier against oxidation and ensures the microstructural uniformity of the nanocluster layer.

2. Low energy μ SR measurements

The sample was bolted onto the cold finger of the cryostat in the low energy muon apparatus [3]. The low energy muons were implanted at normal incidence to the sample; their initial spin-polarisation was approximately parallel to the sample surface. Muons with 20 keV kinetic energy display an implantation profile with a most probable depth of 89 nm and half maxima at 60 nm and 102 nm [4]. Most of the implanted muons stop at random sites in the matrix, in the regions between the clusters. Decay positrons were detected with two orthogonal pairs of scintillators. Transverse field spectra were collected as a function of increasing temperature after field cooling in 10 mT from room temperature. The field was parallel to the incident muon beam. The field was then removed before cooling for the zero field measurements.

It is well known that when the magnetic moments of isolated clusters are static on the timescale of the measurement (approximately 10 μ s), the spectra of the transverse field decay positrons exhibit a pure exponential damping, of the form $\exp\{-(\lambda t)\}$ [1, 6, 7]. Simulations of the dipole field with a cluster concentration of 0.1% showed the expected Lorentzian field distribution $p(B)$ with a half width half maximum of $\Delta B = 0.7$ mT, as shown in Figure 1. ΔB is directly proportional to the saturation moment of the clusters and to the cluster concentration by volume. The damping rate of the muon spectra may be predicted from $\lambda(0) = \Delta B \gamma_\mu$ [1, 7]: $\gamma_\mu = 135.5$ kHz T⁻¹.

When the moments are rapidly fluctuating in orientation with a single relaxation rate $\nu(T) = \nu_0 \exp(-\Delta E/k_B T)$, the damping of the transverse field spectra is described by an exponential raised to the power of a half, i.e., $\exp\{-(\lambda t)^{0.5}\}$ [1, 5, 6]. The damping parameter $\lambda(T)$ is related to the cluster relaxation rate $\nu(T)$ by $\lambda(T) = 4\lambda_0^2/\nu(T)$.

The full circles in Figure 2 show the values of the damping parameter $\lambda(T)$ obtained from fits of the transverse field spectra. Pure exponential damping was used to fit to the spectra collected below 10 K while square root exponential damping was used to fit to the spectra collected above 10 K as discussed above. The broken line shows an average low temperature damping rate of $\lambda(0) = 0.21$ μ s⁻¹. This corresponds to a static distribution of local magnetic fields with a half-width, half maximum of $\Delta B = 0.25$ mT. From this we deduce an effective volume

Figure 1. Simulation of the static dipole field due to iron nanoclusters of saturation moment 2 T at a concentration of 0.1% by volume in an applied field of 10 mT.

Figure 2. Muon damping rate $\lambda(T)$ in zero field (○) and a transverse field (TF) of 10 mT (●). The dotted line shows a low temperature, static relaxation rate of $0.21 \mu s^{-1}$, the full line a linear fit to the TF field data above 10 K.

concentration in the whole sample of 0.04%. This is smaller than expected from the characteristics of the cluster source, and may represent a variation of cluster concentration across the sample area. The full line shows a straight line fit to the high temperature data. The slope and intercept yield an energy barrier of $\Delta E = 37 \pm 4$ K and an intrinsic superparamagnetic relaxation rate of $\nu_0 = 67 \pm 15$ MHz, respectively.

The open circles in Figure 2 show the results of fits to spectra collected in zero field. The spectra were fit with a Lorentzian Kubo function as described elsewhere [6] and the resulting data are seen to be consistent with the transverse field data. This suggests that the 10 mT field applied in the transverse field measurements was negligible in comparison with the anisotropy field of the nanoclusters. It therefore has a negligible effect on the relaxation time. If in future work larger fields and aligned nanocluster assemblies are possible, this finding may be of particular importance, for the cluster relaxation rate is increased by large magnetic fields and is sensitive to the angle between the field and the magnetic anisotropy axis [7].

3. DC magnetisation data

Magnetisation measurements in fields B_{app} of up to 0.1 T and temperatures from 5 K to 100 K were performed in a SQUID magnetometer. The saturation moment was determined from measurements in fields of up to 1.5 T in a vibrating sample magnetometer (VSM). The sample comprised of a nanocluster layer equivalent to 7019 Å of silver and 21 Å of iron prepared on a PEEK substrate of area 5.7 cm². The sample was cut using ceramic-bladed scissors into twelve pieces which were stacked and wrapped in PTFE tape in their original orientation onto the sample

Figure 3. Magnetisation curves at 50 K ($\diamond$) and 100 K ($\circ$).

Figure 4. Magnetisation curves at 10 K ($\diamond$) and at 20 K ($\circ$).

holder, a colourless drinking straw. We saw no evidence for any magnetic anisotropy with the field applied at various in-plane angles or perpendicular to the plane. The data reported here were taken with the field applied in the film plane. The errors in repeated measurements at each point were observed to be of the order of a few percent.

Figure 3 shows SQUID measurements of the magnetic moment of the sample recorded during field sweeps at 50 and 100 K plotted against B_{app}/T . Figure 4 shows the data at 10 and 20 K. The data at 50 and 100 K superpose, as expected for an assembly of superparamagnetic clusters in the low anisotropy limit, i.e., $\Delta E \ll k_B T$. Least squares fits of the Langevin function to these data, using the saturation moment measured in the VSM as a fixed parameter, yielded a moment per cluster of $1961\mu_B$ at 50 K and $1987\mu_B$ at 100 K. We therefore take an average cluster moment of $1974 \pm 13\mu_B$, significantly smaller than the $2267\mu_B$ deduced for the larger clusters in our previous work [1]. Assuming an enhanced moment per iron atom of $2.3\mu_B$, this yields a cluster size of 858 ± 6 atoms. If we assume the bulk number density for iron, $8.49 \times 10^{28} \text{ m}^{-3}$, we obtain a cluster volume of the order of 10^{-26} m^3 and hence, with the energy barrier obtained from the μSR data, a uniaxial anisotropy constant of $K = 5.1 \pm 0.5 \times 10^4 \text{ J m}^{-3}$.

The 10 and 20 K data in Figure 4 do not superpose. In a size-distributed assembly, there is a temperature range in which larger nanoclusters remain blocked while smaller nanoclusters behave as superparamagnets. Superposition occurs when all of the nanoclusters are superparamagnetic (the size distribution does not destroy superposition). Even a monodisperse assembly can show deviations from superposition away from the low and high field limits, due to the magnetocrystalline anisotropy [8, 9]. In these SQUID measurements, superparamagnetism is seen when $T \geq \Delta E/25k_B$, but the Langevin function is derived by assuming that $KV \ll k_B T$ [10]. Calculations of the full response of the assembly require prior knowledge of K , V and $\nu(T)$.

Figure 5. TEM micrograph of iron clusters (dark features) within a silver grain.

Figure 6. High-resolution TEM micrograph showing the silver lattice planes and a single iron nanocluster.

4. TEM data

Figure 5 is a bright-field TEM micrograph taken at 200 kV showing the iron nanoclusters embedded in the silver film matrix. The same film as for the SQUID measurements was used. The matrix consists of small silver grains, which are randomly orientated. Figure 6 shows a high resolution image of the lattice fringes of a silver grain, with an embedded nanocluster. It has not been possible to resolve any crystalline information within the nanoclusters. This may simply be due to the experimental difficulty of achieving a sample orientation satisfying the Bragg condition. The clusters are certainly not spherical, as we assumed in our previous work [1]. The anisotropy we have calculated is best described as uniaxial and dominated by shape. The random arrangement of the clusters produces the lack of anisotropy in the sample taken as a whole. This interpretation is consistent with remanence measurements performed at low temperatures (<2 K) [14].

5. Conclusions

Our μ SR measurements may suggest that clusters prepared by gas condensation exhibit a slower relaxation than those prepared by other routes in other matrices [5, 11]. The relaxation rate is influenced by the “friction” experienced by the thermally activated magnetisation [7]. The equations of motion describing superparamagnetic relaxation are closely analogous to those describing magnetic resonance [12, 13]. There, friction (dissipation) causes the magnetisation to spiral into parallelism with an applied field. Both small and large friction both produce a slow relaxation rate. A more detailed interpretation of our μ SR data thus requires further studies of the crystalline nature of our clusters. There may also be

an interaction between the nanoclusters and the matrix which affects the magnetic anisotropy of individual nanoclusters. The near-perfect lattice match between the silver and iron (100) planes may cause the magnetisation vector to be less free to rotate in some directions than in others.

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