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Magnetization Reversal Measurements of Size-selected Iron Oxide Particles Produced via an Aerosol Route

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We report first measurements of the magnetization reversal of monodisperse 30 nm and 50 nm ferromagnetic Fe_3O_4 particles. These particles are produced in a carrier gas as an aerosol by spray pyrolysis. After production and size selection, they are precipitated on a silicon chip with a niobium SQUID (superconducting quantum interference device) incorporated on its surface. By changing a magnetic field in the plane of the SQUID, we can measure the magnetization reversal of the particles by the flux they induce into the SQUID. The angular dependence of this reversal is determined by rotating the magnetic field around the SQUID. Scanning electron microscope (SEM) images have confirmed the particle size and revealed the position of the collected particles. If the particle concentration is too high, we cannot detect changes in the magnetic moment of a single particle, but measure the magnetic properties of the whole assembly. If only a few particles are found on the SQUID loop the angular dependence of the magnetic reversal of a single particle can be measured; this result is compared with a simple model of magnetization reversal. © 1998 John Wiley & Sons, Ltd.

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INTRODUCTION

The mechanisms of magnetization reversal in small magnetic particles have been much discussed in recent decades and have prompted intense research activities, motivated in particular by applications in magnetic recording technology. However, experiments were performed, in general, on large assemblies of particles, and the dispersion of morphologies, compositions, orientations and separations of the magnetic entities limited the interpretation of the results. More recently, experimental studies of magnetization reversal in individual particles became possible.[1–3] The first reported measurements performed on individual particles were not consistent with simple classical models, e.g. the model of magnetization reversal by uniform rotation proposed by Stoner and Wohlfarth[4] or the model of thermally assisted magnetization reversal over a simple potential barrier initially proposed by Néel[5] and Brown.[6] This disagreement was attributed to the fact that real samples contain defects which could play an important, if not dominant, role in the physics of magnetization reversal. It was suggested that the dynamics of reversal occurs via a complex path in configuration space, and that a new theoretical approach is required to provide a correct description of thermally activated magnetization reversal, even in single-domain ferromagnetic particles. Recent measurements on high-quality particles can be well explained with the Néel–Brown model.[7] At very low temperatures, quantum effects have been observed.[8]

To study experimentally the magnetization reversal of 30 nm and 50 nm Fe_3O_4 particles, we used a planar niobium microbridge dc SQUID (superconducting quantum interference device) on which these particles were collected. A very

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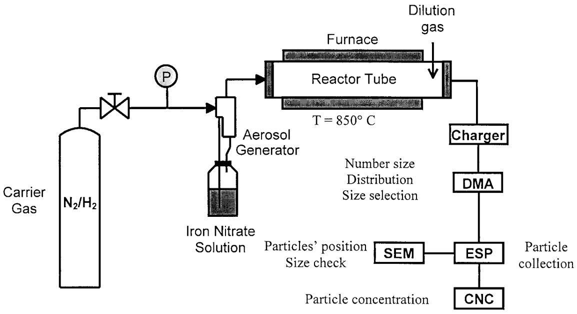

Figure 1 Experimental set-up for particle production, size selection and precipitation.

convenient and easy way to produce monodisperse magnetic particles in the nanometer size range is as an aerosol, i.e. as particles suspended in a carrier gas. In our approach to producing ferromagnetic Fe_3O_4 particles, we used the technique which is known under the name ‘spray pyrolysis’.[9] Details of the formation process are given in the Experimental section. After the size selection, the particles were removed from the gas stream and precipitated on a substrate with the SQUID loops. Some of the particles were found in the SQUID loops, as SEM micrographs revealed. By measuring the magnetic flux through a SQUID loop, one can deduce the magnetization reversal of the particles collected.

In this paper, we report the first measurements and results gained by this novel technique. We also discuss in detail how an atomic force microscope (AFM)[10] can be used as a tool to manipulate the position of collected particles and why this may have the potential to improve future experimental results.

EXPERIMENTAL

To produce nanometer-size particles, we used the spray pyrolysis technique Fig. 1 shows the set-up for particle production, size selection and precipitation. To produce iron oxide particles, we started with a precursor solution of 2.1 g $(Fe(NO_3)_3)\cdot 9H_20$ (Aldrich Chemical Co., purity $> 99.99\%$) in 1 litre of ultrapure water. As the size of the particles produced depends on the mass concentration of the iron nitrate, this concentration was chosen to cover the size range of interest to us. The solution was sprayed in the form of droplets into the gas stream by a constant output atomizer (TSI 3076; TSI Inc.). The droplets were about 800 nm in character. A 93% N_2–7% H_2 mixture was used as the carrier gas at a flow rate of about 3 l/min at room temperature. The gas picked up the droplets and transported them in a mullite tube (i.d. 8 cm) through the hot flow reactor. The reactor was a three-zone furnace (Lindberg 55666) with a heated length of about 90 cm. The reaction temperature in the furnace was about 850°C. Under these reaction conditions, magnetite particles (Fe_3O_4) will most probably be formed[9]. After leaving the reaction tube, the particles were diluted by a factor of about 1:10 to avoid further collisions and water condensation.

The iron oxide particles produced in this way were not uniform in size but showed a log-normal size spectrum. To measure the size distribution and to extract a desired size out of the spectrum, a system diffusion charger – differential mobility analyser (DMA) – condensation nucleus counter (CNC) was used. The diffusion charger is a metal tube in which a radioactive source is placed. The radiation produce negative and positive gas ions, which randomly diffuse onto the surface of the particles. This leads to a well-known charge distribution[11] in which fractions of positively and negatively charged particles as well as neutral particles are present. For particles smaller than 100 nm, the probability of multiple charging is less than 10%. These particles entered the DMA,[12] which was used for size selection. A DMA is a cylindrical condenser, which the particles entered in a laminar flow through an entrance slit close to the outer electrode. A negative voltage applied at the inner electrode forced positively charged aerosol particles into motion perpendicular to their initial flow direction, i.e. towards the centre electrode. In the centre electrode is a small exit slit. Particles having the right electric mobility at a given voltage setting will leave the DMA through this slit. This selection of particles of a given charge is affected only by their particle size and not by particle density. Therefore, the particles leaving the DMA through the exit slit will be of one size with some broadening due to diffusion and the sizes of the entrance and exit slits. The monodisperse particle concentration was then measured by the CNC (TSI 3027; TSI Inc.), which detects individual particles by optical means. By changing the DMA voltage over a certain range, we could measure online the size distribution of the particles. Typical size spectra can be found in Ref. 9.

To precipitate monodisperse particles on a substrate, the DMA voltage setting was kept fixed. The particles leaving the slit were monodisperse and positively charged. They flowed by the collect-

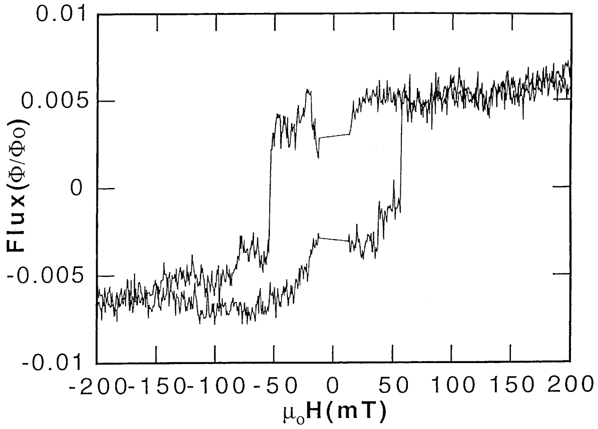

Figure 2 Hysteresis curve for 30 nm particles collected on the SQUID. Φ is the flux induced by the magnetic particles; $\mu_0 H$ is the external magnetic field; Φ_0 is the flux quantum.

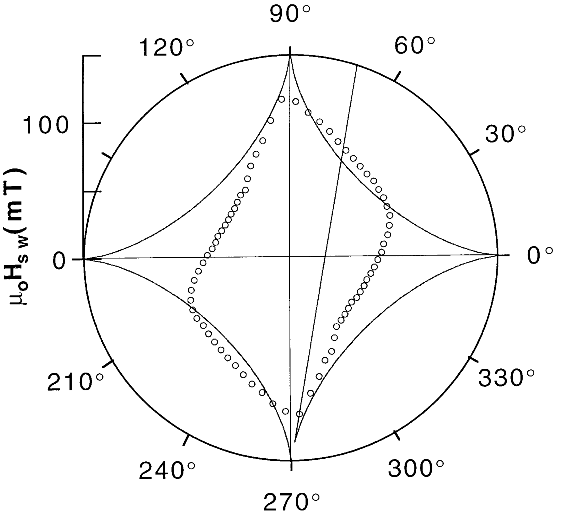

Figure 3 Angular dependence of the switching field for a 30 nm particle. The points (○) represent the experimental data; the line shows the calculation based on the Stoner–Wohlfahrt model.

ing unit, which consists of two electrodes facing each other. The substrate was mounted on the negative electrode. The positive aerosol particles were forced towards the negative electrode and some were precipitated on the substrate. The number of particles removed from the gas in the electrostatic precipitator (ESP) was monitored by the CNC by measuring particle concentration with and without the applied field. The substrate was a silicon chip on which a planar niobium microbridge dc SQUID was implemented. The SQUID was produced by electron beam lithography (JEOL 5DIIU e-beam writer) 1–2 μm in diameter. After exposure of the particle, the substrate was removed from the collector and transferred to the magnetization measurement system.

The SQUID detected the flux through its loop produced by magnetization of the sample. Our method consists of measuring the critical current of the SQUID loop. As this is a periodic function of the flux going through the SQUID loop, one can easily deduce the flux change in the SQUID loop. For hysteresis loop measurements, the external field is applied in the plane of the SQUID; thus the SQUID is only sensitive to the flux induced by the stray field of the sample's magnetization. Due to the close proximity between sample and SQUID, we had a very efficient and direct flux coupling. In this configuration, we could detect magnetization reversals corresponding to 10^4 magnetic moments[13]. We applied the micro-SQUID technique to study the magnetization reversal of individual nanoparticles. Only in the case when a nanoparticle fell on the wire of the SQUID loop was the flux coupling between SQUID loop and particle strong enough to be detected.

After the magnetization measurements, we finally determined the position of the nanoparticles with a scanning electron microscope (SEM; Leo DSM 982 Gemini) equipped with a field emission gun, and rechecked their size.

RESULTS

We report first experimental results of magnetization measurements of size-selected 30 nm and 50 nm Fe_3O_4 aerosol particles deposited on the wire of the SQUID loop. To study the domain structure and the reversal mode of the nanoparticles, the strength of the magnetic field was swept in the plane of the SQUID. The measurements were performed at a temperature $T = 0.1$ K. To obtain results for the angular dependence of the hysteresis loop, these experiments were repeated for different angles between the SQUID and the magnetic field. The angle arbitrarily chosen in the direction along the hard axis of magnetization was 90°. At certain field strengths, we measured discontinuous flux changes corresponding to the flipping of the particle's magnetization (Fig. 2). The corresponding field value is called the 'switching field'. This switching was in all cases faster than 100 μs, the time between two measurements of the flux.

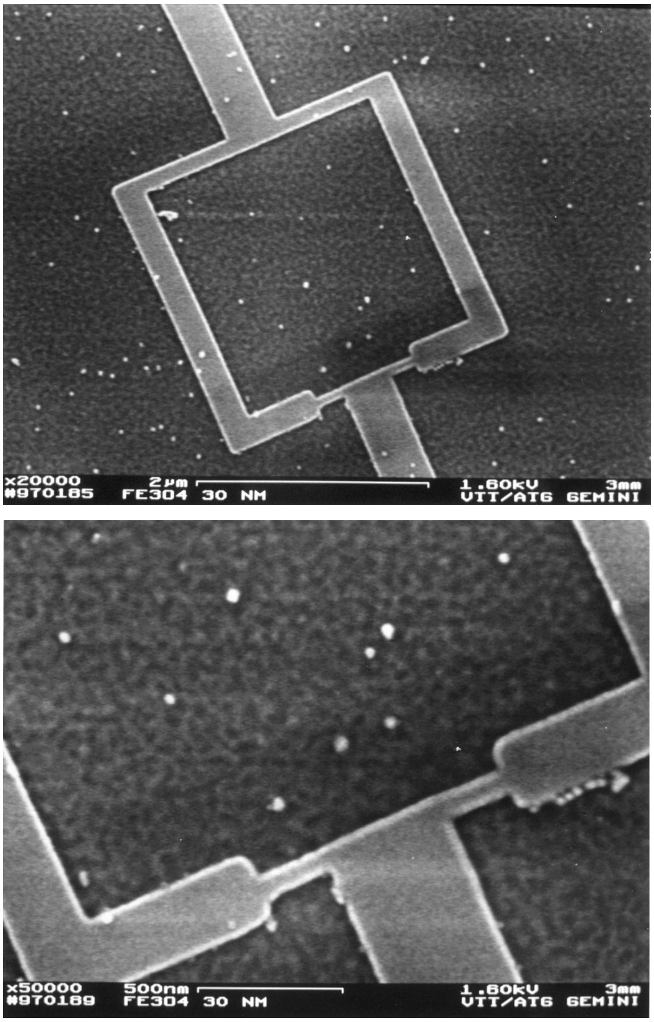

Figure 4 SEM images with different magnifications of the SQUID on which the magnetic measurements for the 30 nm particles were performed.

Sometimes, during one sweep we could observe several switching fields, indicating that more than one particle contributed to the change in flux. However, there is only one particle which caused the largest change. This signal was followed by rotating the field direction around the SQUID; hence the angular dependence of magnetization of this particle could be measured (Fig. 3). However, as there was more than one particle on the SQUID, we did not know which particle was being measured. SEM images taken from the SQUID are shown in Figs 4(a) and 4(b). They confirm that several particles were collected on the loop and attached around it. We compared our result of angular dependence of magnetization with the simplest model of magnetization reversal: i.e. the model of uniform rotation of magnetization as proposed by Stoner and Wohlfarth[4] (see the continuous curve in Fig. 3). The basic hypothesis of the uniform rotation model is that the magnetization of the particles has a constant modulus and the anisotropy energy depends only on the angle between the magnetization of the particles and its easy axis of magnetization. This assumption is only approximately valid. The main deviation is due to the fact that the easy axis of magnetization of the particle did not lie in the SQUID plane, which can be seen by the rounding of the curve near 0°.

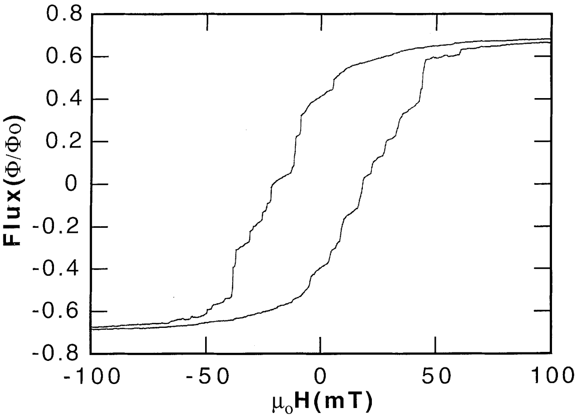

Figure 5 Hysteresis curve for 50 nm particles. The curve is composed of many small steps stemming from individual particles. As the particle concentration around the SQUID is too high, no magnetic signal can be obtained from a single particle.

Furthermore, the asymmetry may be due to the misalignment between shape anisotropy and crystalline anisotropy.

Figure 5 shows a hysteresis curve taken from size-selected 50 nm particles. It shows many very close steps and no signals from individual particles can be resolved. Figure 6 is the SEM image of the corresponding SQUID. Clearly, too many particles are gathered around the SQUID, so that many of them may contribute to the magnetic signal. The high particle density next to the SQUID may be explained by the strength of the electric field, which is highest around the conductive niobium wires. If the sampling voltage was too high, the electric field forced the charged particles towards the wires. Also, some of the particles may be pushed accidentally by the AFM towards the SQUID. In these cases, we did not measure magnetization reversals of single particles but of particle assemblies.

Our measurement is sufficiently sensitive to track the magnetization reversal of a single magnetic particle and follow its angular dependence. However, other particles collected on the loop may interfere to this signal and if particle coverage is too high, the information from individual particle magnetization is lost.

To increase further the sensitivity in order to measure the magnetization of individual particles, we are planning to improve our technique in two ways:

(1) To avoid collection of particles mainly around the wire because of the electric field, the particle will be collected by impaction. The particles in the gas stream will be guided at high velocity through a nozzle below which the silicon chip is mounted. Some of the particles will not follow the gas stream and will impinge on the chip. This should lead to a more evenly distributed coverage of particles on the substrate, as an electric field does not affect their position.
(2) In future measurements, we will use an AFM to

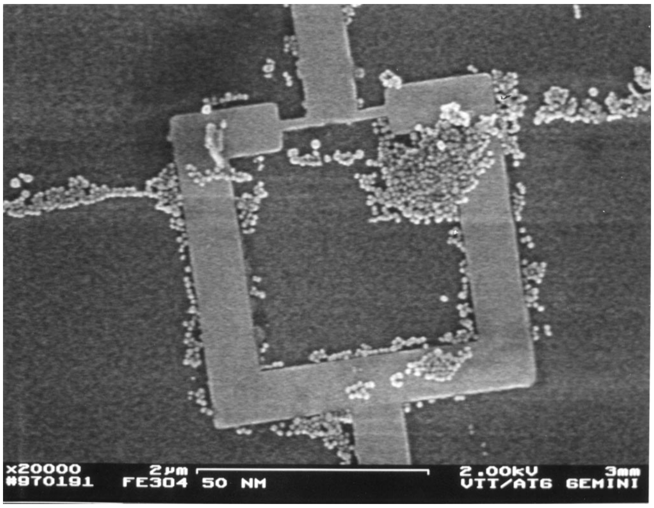

Figure 6 SEM micrograph of the SQUID on which the 50 nm particles were collected confirms the high particle concentration near the SQUID.

move particles over the silicon surface. It is well known[14] that the tip of the microscope can push particles over a smooth substrate. This is sometimes an undesirable phenomenon as it may complicate the imaging of particles, but it can be used to position particles in designated spots on the surface.[15] For further study of individual particles, we developed a technique to move particles on the loop of the SQUID in a controlled way. First, the AFM senses the surface and locates the particles. After finding their position, the AFM tip is brought behind the desired particle, the tip–surface distance is decreased and the particle is pushed to the desired spot. Subsequently, the tip–surface distance is increased again and the particle is released. Recent experiments showed that we were able to move particles in a controlled way with particle sizes down to 10 nm (AFM: Autoprobe CP, Park Scientific Instruments). This technique could also be used if the SQUID was exposed to too many particles. In this case, the AFM can clean the area from the unwanted particles and leave single particles on the loop. In addition to the potential to position the particles, the AFM can be used to image the surface and to support the SEM images with three-dimensional maps.

SUMMARY

In this paper, we have presented a novel technique to produce size-selected magnetic nanoparticles and to measure their magnetic reversal. Fe_3O_4 particles were produced in an H_2–N_2 mixture by spray pyrolysis. After size selection, they were precipitated on a silicon substrate on which a niobium SQUID was imbedded by electron-beam lithography. The magnetic reversal of particles collected on the SQUID was measured by the flux they induced into the SQUID by switching the direction of an external magnetic field. At particle concentrations that were not too high, the signal of individual particles could be followed and the angular dependence of magnetization reversal was measured and compared with the Stoner–Wohlfahrt model, a simple model of magnetization. At particle concentrations that were too high, the magnetic properties of individual particles could not be resolved but the magnetic reversal of the monodisperse assemble was measured. We have discussed the future use of a new collection technique which should help to distribute the particles more evenly on the substrate, and an AFM as a tool to manipulate the positions of the particles on the substrate. In future experiments, we will systematically select particle sizes over a wide size range and, as various particle species can be produced by an aerosol routine, we will extend our research to measure the magnetic properties of particles from different materials.

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