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Magnetic Properties of Deposited Iron Clusters Produced in a High-yield Laser Vaporization Source*

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Clusters of iron produced in a laser vaporization source have been characterized with time-of-flight spectra and deposited on different substrates for production of films of varying thickness. The magnetic properties of these films with thicknesses of 60 and 120 nm were investigated using an alternating gradient magnetometer. The films exhibit mono-domain behavior from a broad size distribution which has been confirmed by transmission electron microscopy. Films were also investigated by Mössbauer spectroscopy, which showed fast relaxation in the particles at room temperature.

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INTRODUCTION

Cluster-based materials can be used for studies of the magnetic properties of particles with diameters smaller than several tenths of a nanometer. This corresponds to the critical size for a spherical ferromagnetic particle to consist of a single domain.[1] These small particles are of great physical and technological interest today. They can be used, for example, as model systems for investigating fundamental magnetic properties[2,3] and in applications as components in high-density memories. Depending on the temperature, one often encounters the superparamagnetic effect. This arises from the fact that the energy to change the direction of the small moment of the particles is comparable with the thermal energy. The magnetization of non-interacting mono-domain particles fluctuates over an energy barrier with a characteristic relaxation time dependent on the thermal energy.[4] Particles of which the magnetization fluctuates faster compared with the experimental measuring time are superparamagnetic, while particles with a slower relaxation time are said to be thermally blocked.[5] Superparamagnetic particles do not show coercivity or remanence, whereas thermally blocked particles do.

We are now developing a high-yield laser vaporization source which is capable of producing films of clusters. The cluster source operates with a continuous flow of helium gas. This is dissimilar to the traditional pulsed laser vaporization source from Smalley's group[6] and the earlier source from our group[7] where a pulsed gas flow is used. The source is designed to use vaporization lasers with high repetition frequency. In this work we used an ArF excimer laser (λ=197 nm) with a repetition frequency of 90 Hz. The distribution of clusters was monitored with a time-of-flight spectrometer and the yield was monitored with a quartz microbalance. Films of iron clusters approximately 60–120 nm thick were grown with an area of typically 1 cm^2 and the magnetic properties of these films were studied.

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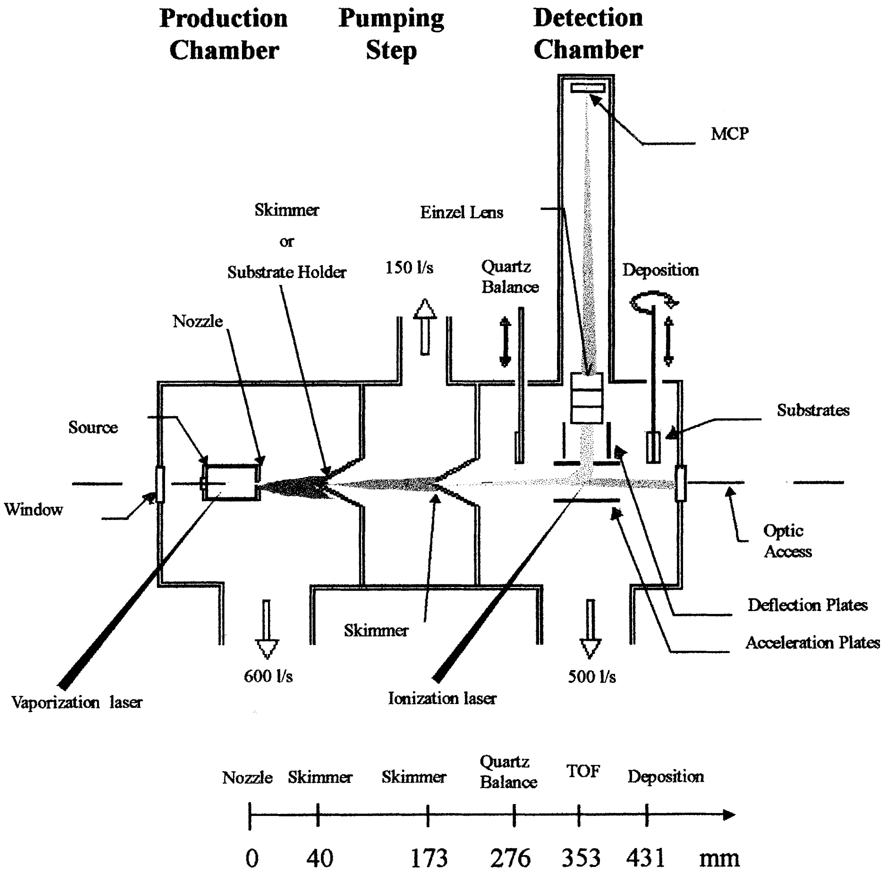

Figure 1 The experimental set-up showing the distances between the nozzle, skimmers, quartz balance, time-of-flight spectrometer and deposition unit.

EXPERIMENTAL

Clusters

The clusters were produced in a recently developed high-yield laser vaporization cluster source; see Fig. 1. A high-intensity laser beam was focused on the target surface to produce a hot metal plasma in the cluster source. The target was a pure square metal sample which moved in the *x* and *y* directions in order to expose a fresh metal surface and obtain stable cluster production. The vaporized plasma was transported in a continuous flow of 30 mbar He through a 0.7 mm diameter flat nozzle into the production chamber with a background pressure of 10^{-2} mbar. This chamber was pumped by a turbo molecular pump with an effective pumping speed of 600 l s^{-1} at this pressure. The cluster beam then passed through a 1 mm diameter skimmer to a differentially pumped region kept at 10^{-5} mbar by a turbo molecular pump with the effective pumping speed of 150 l s^{-1}. Finally, the clusters entered the detection chamber through a second 2 mm diameter skimmer. This chamber was pumped by a 500 l s^{-1} turbo molecular pump and operated at a pressure of 10^{-7} mbar. The detection chamber was equipped with a linear time-of-flight mass spectrometer (TOFMS), a quartz balance (MaxTech Inc.) and a deposition unit. The quartz balance was used to measure the absolute amount of clusters in the beam. The total mass of the layer and the deposition rate were determined. The quartz balance was located just in front of the TOFMS and the position of the unit could be manipulated from outside the vacuum system. The set-up was constructed so that a section for size selection of clusters could be installed after the second skimmer and before the TOF section.

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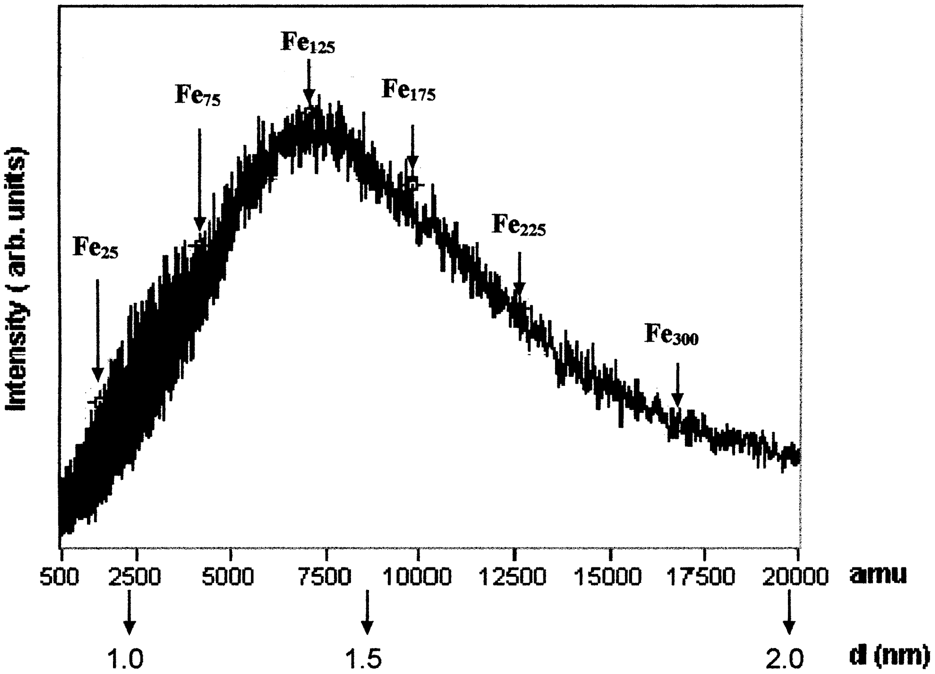

Figure 2 Mass spectra representing the size distribution for free iron clusters in the beam. The mean size is Fe_{125} with a diameter $d = 1.4$ nm.

In the present set-up the neutral cluster beam was photo-ionized in a static electric field with the light from an ArF laser. The charged clusters were accelerated perpendicularly to the neutral beam and directed onto the micro channel detector through a pair of deflecting plates and an einzel lens. The mass spectra were recorded in a digital oscilloscope (LeCroy 9400), stored and analyzed in a computer. A time-of-flight spectrum was recorded; see Fig. 2. A Nd:YAG laser ($\lambda = 355$ nm) and the repetition frequency used for vaporization was 10 Hz. The mass spectrum shows a broad size distribution, with a center peak near Fe_{125}. The beam of clusters contains sizes from a few atoms up to about a few hundred. The diameters of the free clusters are approximately 0.5–2 nm.

The depositions are performed at room temperature on several different substrates. Thin films of up to 10 nm are fabricated in the deposition unit located behind the acceleration plates of the TOFMS. During a deposition process the quality of the cluster beam is controlled by the TOFMS. As can be seen in Fig. 1, the quartz balance cannot be used to measure the deposition rate at the same time as a deposition is being carried out. Therefore, the quartz balance is used to measure the deposition rate before and after each deposition, and the thickness of the film is determined from the deposition time.

Film layers with thicknesses from 10 to 200 nm are fabricated in the production chamber (we have observed that films thicker than 200 nm are cracked, probably because of stresses in the films produced.) The first skimmer can be removed and replaced by a substrate holder. The substrate is located 40 mm from the cluster source nozzle and the diameter of the deposition spot is about 5 mm. A wide beam is advantageous in this particular case because it makes it possible to cover a large substrate. The TOFMS and the quartz balance can only be used indirectly when these depositions are performed.

In this study, we needed to produce films 50–100 nm thick in order to obtain accurate magnetization measurements. Therefore, the samples were fabricated in the production chamber. Using an ArF excimer laser as vaporization laser minimized the deposition time. This was our fastest available laser, with a repetition frequency of up to 90 Hz. At a repetition frequency of 90 Hz the deposition rate was estimated to be 3.7 Å s^{-1} for the iron clusters in the production chamber (Fig. 1). It took approximately 5 min to produce the layer 120 nm thick.

The size distribution for ArF-produced clusters

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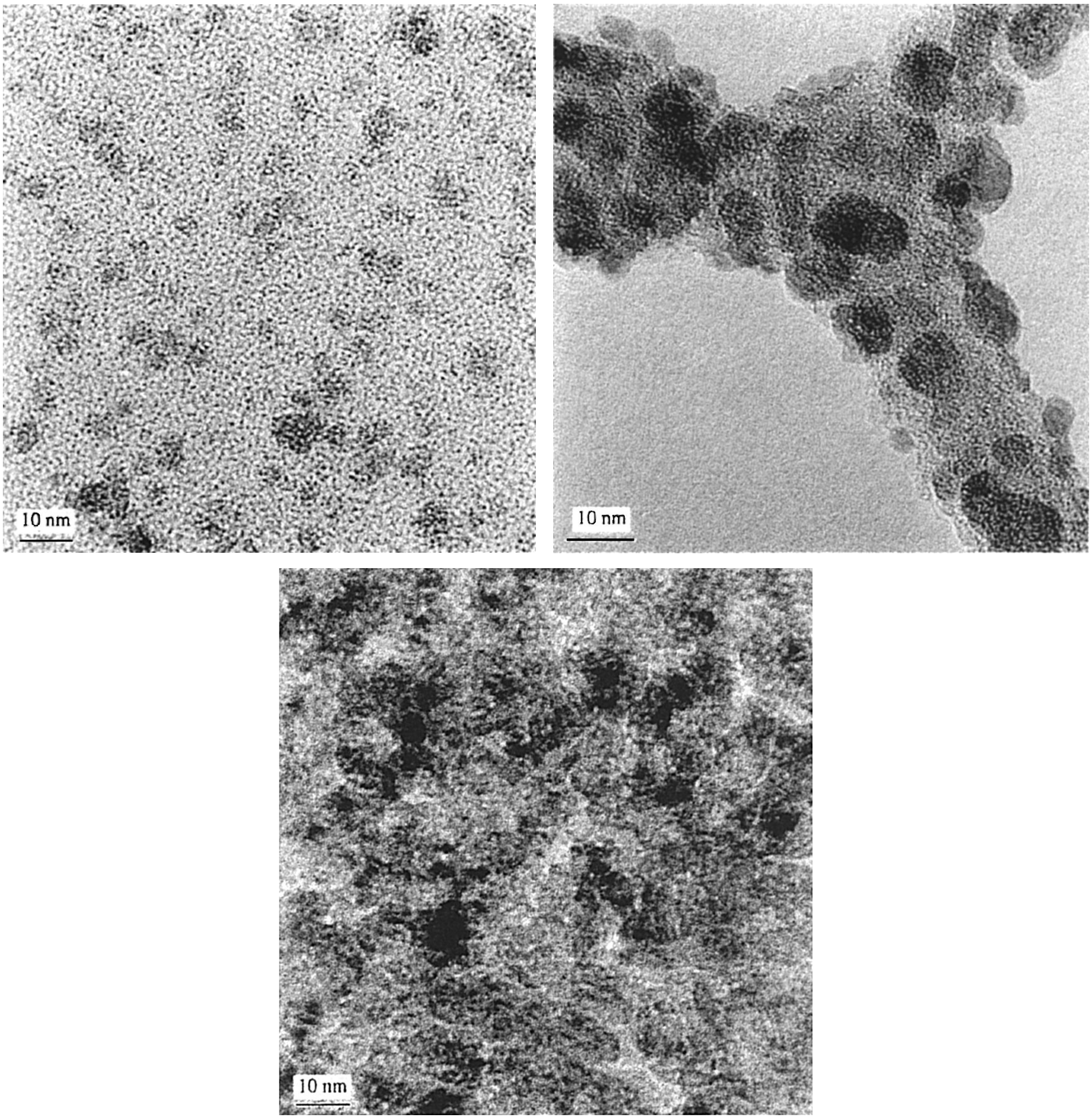

Figure 3 TEM images of Fe clusters as deposited on a lacey carbon film with increasing layer thickness, showing the sequential growth of a nanoporous film: (a) dispersed clusters (layer thickness 0.5 nm); (b) clusters and cluster aggregates (5 nm); (c) nanoporous film (50 nm).

has not been measured here, but we expect a similar size distribution as for clusters produced with an Nd:YAG laser.

It is known that small clusters can aggregate to larger particles on a substrate. In this case, the size distribution on the substrate is different from that observed in the time-of-flight spectrometer, which will give different nanostructures than those expected from the mass spectra. These aggregation effects have been studied by transmission electron microscope (TEM). Iron clusters with layer thicknesses of approx. 0.5, 5 and 50 nm were deposited on carbon films on copper grids. The three TEM pictures (Figs 3a, 3b and 3c) show the sequential growth of a nanoporous film. Figure 3(a) shows the particles produced from the cluster source. The smallest cluster sizes are not visible here because the carbon film is too rough. There are larger

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particles of up to 5 nm diameter present on the film which could be explained as cluster colloids or directly evaporated products from the source. Figure 3(b) shows larger particles than Fig. 3(a), which illustrates that particles have probably aggregated. A broad size distribution from a few nanometers up to 10 nm is observed and the particle surfaces show facets. In Fig. 3(c) the layer is not uniform and the result is a nanoporous film.

Sample preparation

In order to study the variation of the magnetization over the sample area and the stability of the material over time, one sample with diameter 10 mm was deposited on a microscope coverglass. Two other samples with diameter 3 mm were prepared and deposited on micro slides; sample A with a total mass 5.8 μg of clusters and sample B with 2.6 μg. This corresponds to bulk iron films of thickness 117 and 58 nm, respectively. The magnetic properties of these samples were measured immediately after preparation.

Magnetic measurements

The magnetic measurements were performed with an alternating gradient magnetometer from Princeton Measurements Corporation. Hysteresis loops were measured in the field range ± 2 T at temperatures between 10 and 295 K. The measured magnetic moment was corrected for the diamagnetic background due to the substrate and the sample holder. The final results were obtained as magnetic moment per unit of mass, M, by dividing this corrected value by the mass of the sample. The films were also characterized by Mössbauer spectroscopy.

RESULTS AND DISCUSSION

The magnetization saturated in fields above about 0.5 T for all the samples. The saturation magnetization, M_s, was determined from the value measured at 1 T. The coercive field, B_C, and the remanence, M_r, were determined from hysteresis loops performed in the range ± 0.5 T. Figure 4 shows two of the hysteresis curves measured for sample A at 30 and 295 K. The shape of the hysteresis loops was observed to change slowly with time; M_s decreased by about 15% after one week in the ambient atmosphere and M_r also decreased while B_C increased. Similar behavior has been observed in other Fe particles;[8] the effect may be explained by partial oxidation of the sample. The hysteresis curves of samples taken from different parts of the 10 mm cluster sample became overlapping when they were normalized to their saturation values. This implies that although the sample grows thicker at the center of the cluster beam, the distribution of cluster sizes remains the same. For sample A the measurements yielded $M_s = 200\ \mathrm{A\,m^2\,kg^{-1}}$, practically independent of temperature. This is the same value as that of α-iron, with a saturation magnetization of about $210\ \mathrm{A\,m^2\,kg^{-1}}$. The M_s value of sample B was $172\ \mathrm{A\,m^2\,kg^{-1}}$, which is reduced by 20% with respect to the expected value for particles of α-Fe. This could possibly be explained by the fact that the particles in a thinner film are more easily oxidized. The shape of the hysteresis curves was observed to depend on the measuring time and the temperature. The coercivity field increased from $B_C = 7.0$ mT at 295 K to 91.9 mT at 30 K. The remanence increased from $M_r = 44\ \mathrm{A\,m^2\,kg^{-1}}$ at 295 K to $148\ \mathrm{A\,m^2\,kg^{-1}}$ at 30 K. The temperature

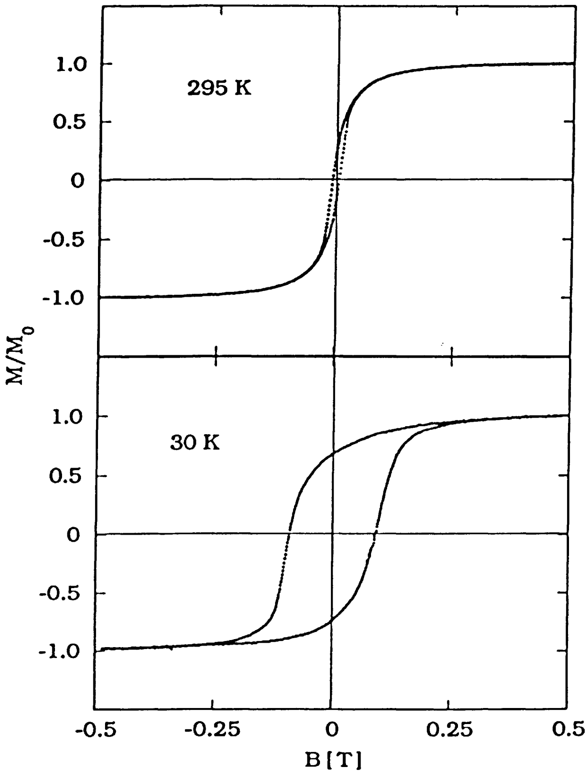

Figure 4 Normalized hysteresis loops at 295 and 30 K of sample A. M_0 is the magnetization at 0.5 T.

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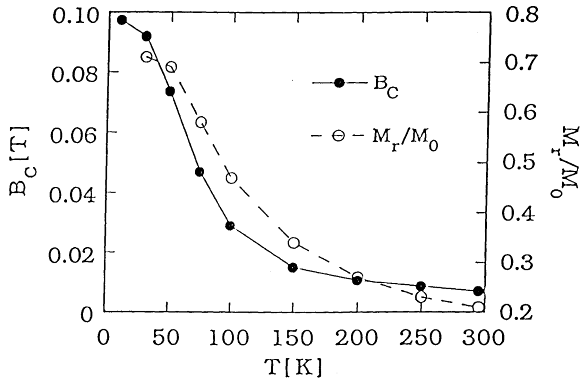

Figure 5 Coercive field B_c (solid line) and normalized remanence M_r/M_0 (broken line) versus temperature of sample A. M_0 is the magnetization at 0.5 T.

dependence of B_C and M_r for sample A in the temperature range 10 to 295 K can be seen in Fig. 5. The observed increase of B_C and M_r with decreasing temperature is typical for mono-domain magnetic particles where the magnetic moments of the particles become thermally blocked below a specific temperature, depending mainly on the volume and thus the anisotropy of the particles.[5] The fact that B_C and M_r vary with the temperature over the whole temperature range suggests that there may be a broad distribution of cluster sizes, which was confirmed by the mass spectra and TEM data. Thus, the magnetic measurements show that the samples comprise mono-domain particles with a broad size distribution.

A sample 100 nm thick has been studied by Mössbauer spectroscopy at room temperature. Although the statistics for this measurement is not sufficient, the first analysis of spectra shows the typical characteristics of fast superparamagnetic relaxation. The sample seems to be α-iron and no oxidation products are present. Depositing films with ^{57}Fe clusters in order to increase the signal and study Mössbauer spectra at lower temperatures will follow the present work. We also expect to obtain more information about the oxidation process.

CONCLUSIONS

The deposited iron clusters show typical mono-domain behavior in the magnetization measurements and Mössbauer spectroscopy. The size distribution is broad, according to the observations made by TEM. Clusters with sizes from 2 to 10 nm are present which should be compared with the 0.5 – 2 nm size distribution observed by TOF spectra. It is possible that iron clusters coalesce to larger particles on surfaces. It is also a consideration that larger aggregates are formed directly from the laser ablation and ejected onto the substrate. These particles are too heavy to be observed in the TOF spectra. The broad size distribution is confirmed by the magnetization measurements, where B_C and M_r vary with the temperature over the whole temperature range measured. It has also been found that the saturation magnetization decreases slowly with time, probably because of oxidation.

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REFERENCES

1. C. Kittel, *Phys. Rev.* **70**, 965 (1946).
2. M. Hanson, C. Johansson and S. Mørup, *J. Phys.: Condens. Matter* **7**, 9263 (1995).
3. M. Hanson, C. Johansson, M. S. Pedersen and S. Mørup, *J. Phys.: Condens. Matter* **7**, 9269 (1995).
4. L. Néel, *C.R. Acad. Sci. Paris* **228**, 664 (1949).
5. C. P. Bean and J. D. Livingston, *J. Appl. Phys.* **30**, S120, (1959).
6. T. G. Dietz, M. A. Duncan, D. E. Powers and R. E. Smalley, *J. Chem. Phys.* **74**, 6511 (1981).
7. J. L. Persson, M. Andersson and A. Rosén, *J. Phys. Chem.* **100**, 12222 (1996).
8. S. Gangopadhyay, G. C. Hadjipanayis, C. M. Sorensen and K. J. Klabunde, *IEEE Trans.* **29**(6), (1993).