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Magnetization and Mössbauer study of partially oxidized iron cluster films deposited on HOPG

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ABSTRACT

Iron clusters produced in a laser vaporization source were deposited to form cluster-assembled thin films with different thicknesses on highly oriented pyrolytic graphite substrates. The development of oxidation of the clusters with time, up to three years, was investigated by magnetic measurements using an alternating gradient magnetometer. Furthermore, to receive information about the oxidation states, clusters of ⁵⁷Fe were studied using Mössbauer spectroscopy. The magnetic analysis shows a time evolution of the saturation magnetization, remanence, and coercivity, determined from the hysteresis curves characteristic of a progressing oxidation. The different thicknesses of the iron cluster films as well as a protective layer of vanadium influence the magnetic properties when the samples are subjected to oxidation with time. While the saturation magnetization and remanence decrease and reach half the initial values for almost all the samples after three years, the coercivity increases for all samples and is more substantial for the thickest sample with a vanadium protective layer. This value is three folded after three years. Furthermore, based on a core-shell model and using the saturation magnetization values we have been able to quantitatively calculate the amount of the increase of Fe-oxide as a function of time. The Mössbauer spectroscopy shows peaks corresponding to iron metal and maghemite.

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1. Introduction

There is a great interest in nano-sized materials both from a fundamental point of view and for applications. The fundamental properties that are studied are e.g., the size dependence of the magnetic properties [1,2] or the reactivity, in particular the phase stability under different conditions, whereas possible applications range from new functional materials to biomedical diagnostics and therapy [3–6]. Also magnetic and structural properties of self-assembled iron-oxide nanocrystals with different shapes have also attracted huge interests due to their applications [7–11].

In the present study, the stability of iron clusters prepared in a cluster deposition system [12,13] and their magnetic properties as function of oxidation time are investigated by means of Mössbauer spectroscopy and magnetization measurements using

an alternating gradient magnetometer (AGM). Other studies related to oxidation processes of magnetic nanoparticles of ferromagnetic materials such as Fe and Co and the changes in their magnetic properties when the nanoparticles are oxidized have been reported [14–21]. The oxidation process leads to an oxidized surface layer that grows on the ferromagnetic core. The degree of changes in the magnetic properties depends on the size of the ferromagnetic core and the amount of oxidation layer on the nanoparticles.

The properties of magnetic nanoparticles can differ considerably from bulk materials. Some particle size effects are related to the fact that the thermal energy may be comparable to the magnetic anisotropy energy (the energy required to rotate the magnetization direction) that is proportional to the volume of the nanoparticle. The relatively large number of atoms close to the surface with respect to the total number of atoms in the nanoparticles may also have a significant influence on the properties of nanoparticles.

Macroscopic ferromagnetic nanoparticles are spontaneously divided into magnetic domains with different magnetization

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directions, thus minimizing the magnetostatic energy. Formation of domain walls, however, also requires magnetic energy. Therefore, the energy necessary for the formation of domain walls may be larger than the lowering of the magnetostatic energy, if the particle size is below a critical single-domain size. The critical size is typically of the order of 10–100 nm, depending on the magnetic anisotropy energy, the exchange-coupling strength, the magnetization of the material and the geometry of the particles.

As mentioned previously, the magnitude of the anisotropy energy is proportional to the particle volume, meaning that for nanoparticles the magnetic behavior depends drastically on the size of the nanoparticles at a specific temperature. There is a non-zero probability that the magnetization vector is not oriented along one of the easy directions, and that the thermal energy is large enough for the magnetization vector to overcome the energy barrier separating two easy directions [22–24]. If the relaxation time of magnetization reversal is fast compared to the measuring time, the particle is defined as superparamagnetic [25], leading to superparamagnetic relaxation. As the temperature decreases, the thermal energy will at the blocking temperature, which depends on the time scale of the experiment, not be sufficient to overcome the energy barriers and the spins become frozen. The blocking temperature can be measured with both DC and AC magnetic measurements and Mössbauer spectroscopy where the two different techniques have different measurement time scales and the relaxation behavior can be studied in detail. The influence of the superparamagnetic relaxation on the Mössbauer spectra depends on the relaxation time compared to the time scale of the measurement (which is approximately given by the Larmor precession time of the nuclear magnetic moment in the magnetic hyperfine field and is in the range of nanoseconds). If the relaxation time is long enough, i.e. the sample is below the blocking temperature, a magnetically split Mössbauer spectrum appears, in the case of ^{57}Fe with the typical six line pattern. If the relaxation time is short, a superparamagnetic spectrum, with one or two lines, is observed. In the intermediate range, complex spectra with broadened lines can be expected. In practice, a sample of small particles always has a particle size distribution. At a given temperature, some particles may therefore be below their blocking temperature, whereas others may be above it. Therefore, Mössbauer spectra of magnetic nanoparticles often contain both a magnetically split component and a superparamagnetic component. The area ratio of the two contributions varies as a function of temperature and gives information on the

particle size distribution. When the relaxation time is larger than the measurement time scale in magnetic quasistatic measurements (with the measurement time scale typically in the range of 10 s) we will obtain remanence and coercivity in the hysteresis loops. When the relaxation time is shorter than the time scale of the magnetic measurements, the nanoparticles are superparamagnetic with no remanence and coercivity.

Magnetic particles with nanometer dimensions can be produced by various chemical and physical methods [26,27]. The aim is to control and vary the average size, where single-domain and/or superparamagnetic behaviour occurs, and to keep the size distribution of the particle ensemble narrow. In this project we have produced cluster-assembled iron films by deposition of clusters onto a substrate, which is an alternative method for magnetic nanoparticle film production [28]. The characterization of magnetic properties from hysteresis loops has been described in previous publications [12,13]. In this paper we have taken a step further through production of cluster-assembled films of different thicknesses and also films covered with layers of vanadium clusters. All the films have been investigated with an AGM for studies of the oxidation processes and a representative sample enriched in ^{57}Fe has been studied with Mössbauer spectroscopy for detection of the resulting magnetic phases.

2. Experimental setup and procedures

2.1. Apparatus for cluster deposition

The clusters were produced in a laser vaporization cluster source [12]. The apparatus has a three-section vacuum chamber shown schematically in Fig. 1.

Cluster formation takes place in a 10 mm diameter cavity through which there is a continuous flow of He gas at a pressure of approximately 2500 Pa. Pulsed laser light is focused onto the target, and the evaporated metal atoms and ions condense into clusters and leave the cavity through a 0.7 mm diameter flat nozzle. From the production chamber, with a pressure of 1 Pa, the cluster beam continues through a 1 mm diameter skimmer into a differentially pumped region at 10^{-3} Pa. After passing a second skimmer with 2 mm diameter the cluster beam finally enters the detection chamber at 10^{-5} Pa. In this chamber the cluster beam is photoionized and the cluster ions are accelerated into a linear time-of-flight (TOF) mass spectrometer to verify cluster formation and characterize the size distribution. A typical mass spectrum is shown in Fig. 2.

To vaporise the metal, the second harmonic ($\lambda=532$ nm and a pulse energy of up to 75 mJ/pulse) of a Nd:YAG laser with a repetition rate of 10 Hz was used, and an ArF excimer laser ($\lambda=193$ nm) provided the light for ionization. The target was a square metal plate (25×25 mm²) that was continuously moved to expose a fresh surface to the laser beam. To optimize the signal sensitivity in the Mössbauer analysis, we used iron targets of enriched ^{57}Fe in the shape of a thin film that was glued onto a thicker plate.

In this study, the depositions, on highly oriented pyrolytic graphite (HOPG) substrates at room temperature (RT), were performed in front of the first skimmer, 20 mm from the nozzle. The substrate was mounted on a plate attached to a simple manipulator based on magnetic coupling through a glass viewport. Thus, mass spectra were recorded both before and after the deposition by moving the substrate in and out of the beam. At the position of the deposition, a quartz crystal microbalance (QCM) could be transferred into the cluster beam. In this way the deposition rate could be measured just prior to and after deposition. The QCM might not give exact absolute values, since the film

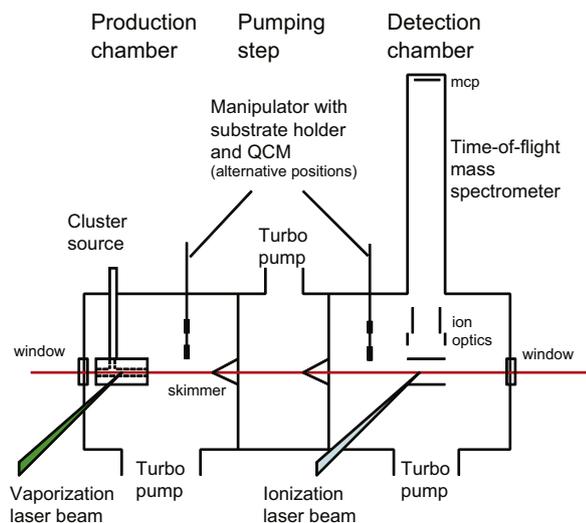


Fig. 1. Apparatus for iron clusters production.

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