# Magnetic properties of nanoscale iron particles

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Nanoscale iron particles have been prepared by iron atom clustering in cold pentane. Particle growth was terminated by adsorption of oleic acid, yielding air stable particles ranging in size from 2 to 12 nm, that were amorphous according to XRD analysis. TEM analysis showed that the larger particles were prolate spheroids while the smaller ones were spherical. The as-prepared sample had a room-temperature saturation magnetization of $M_s = 12.3$ emu/g and a coercivity of $H_c = 60$ Oe. Following heat treatment under argon, the XRD results showed the following reaction scheme; oxidation to $Fe_3O_4$ at 360 °C and reduction to $\alpha$-Fe at 520 °C (processes apparently due to adsorbed oleic acid). For the 520 °C treated sample, the room-temperature saturation magnetization and coercivity were $M_s = 200$ emu/g and $H_c = 20$ Oe, respectively. By pentane washing of the as-prepared sample, the smaller particles could be separated by filtration leaving the larger 8–12 nm particles on the filter. This powdered sample trapped on the filter had $M_s = 54.9$ emu/g and $H_c = 60$ Oe. Heat treatment of this sample also caused oxidation to $Fe_3O_4$ at 360 °C and an incomplete reduction to $\alpha$-Fe and FeO at 520 °C. For the 520 °C treated sample, the recorded room-temperature saturation magnetization and coercivity were $M_s = 123.6$ emu/g and $H_c = 20$ Oe, respectively.

## INTRODUCTION

The preparation and properties of very small particles often called "clusters" or "nanoscale materials" have been of great interest in recent years.[1] Particles of 1–100 nm often exhibit hybrid properties different from molecular or atomic, and different from the bulk solid state.

Our approach has been to deposit metal atoms into low-temperature organic solvents, which leads to atom clustering moderated by solvation [solvated metal atom dispersion (SMAD)].[2] For magnetic materials prepared by similar methods, three factors have been found to affect their magnetization: surface oxide formation, inhomogeneous particle size distribution, and carbonaceous fragment inclusion within these particles[3-5] The nature of these problems implies that they might be solved by varying the metal-solvent interaction. Recently, Timms and co-workers,[4] using metal atom deposition/clustering in liquids, have reported that they were successful in controlling some of these problems by adding a surfactant to the host solvent during metal evaporation. This modification in their method closely follows the preparation of ferrofluids.[6]

In this paper we report that we have successfully generated nanoscale iron clusters trapped and protected by adsorbed oleic acid. These particles are air stable and can be separated into superparamagnetic and ferromagnetic fractions by filtration/washing techniques.

## EXPERIMENT

Our metal atom (vapor) reactor has been described elsewhere.[7,8] A solvent inlet with two ports was used in this work so that initially iron atoms and pentane vapor could be codeposited at 77 K. Later a pentane-oleic acid solution was added as a liquid solution. (Fe: pentane: oleic acid was 1:40:2 molar ratios.) After allowing the reaction chamber to slowly warm to room temperature, the sample was collected by vacuum syphoning onto a fritted filter under pure argon. Filtration and washing with more pentane yielded two fractions. The ferromagnetic fraction remained on the frit as a black powder while the superparamagnetic fraction filtered through and formed a colloidal suspension (ferrofluid in pentane).

Heat treatments were carried out in an autoclave at 386 and 520 °C for 6 h under flowing argon. A SQUID magnetometer was used to determine magnetic properties (weighed samples were imbedded in paraffin), and a high-temperature VSM to obtain Curie temperatures. Other techniques, such as TEM, DSC, and XRD were also used to determine size and morphologies of these particles.

## RESULTS AND DISCUSSION

Iron atoms were codeposited with pentane vapor to form a dark colored matrix at 77 K. Then a pentane-oleic acid solution was allowed to freeze on top of the matrix. Upon warming the iron atoms agglomerated to clusters, which were trapped and stabilized by the oleic acid. This sample was labeled 1.

Figure 1 illustrates magnetization as a function of applied field for sample 1. The room-temperature magnetization at a field of 55 K Oe was only 12.4 emu/g as compared to the bulk iron metal value of 200 emu/g.[9] Sample 1 was air stable; presumably due to protection by adsorbed oleic acid. The values determined from the temperature dependence studies of the coercivity were $H_c = 1260$ Oe at 10 K and decreased to 60 Oe at 300 K. These high values might be due to a phenomenon called "exchange anisotropy" which describes the spin coupling at the interface of these iron particles and the organic coating.[10-12]

XRD analysis of sample 1 showed that it was amor-

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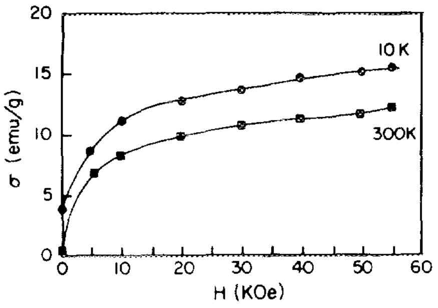

FIG. 1. Magnetization as a function of the applied field for sample 1.

phous. The TEM micrograph measurements showed particles ranging in size from 2 to 12 nm in diameter that resembled distorted spheres. The temperature dependence of the magnetization and the Curie points were measured and showed, with increasing temperature, a phase change at 360 °C and an additional phase change around 600 °C. Two Curie points at 589 °C and 760 °C were measured by extrapolation for these two phases.

Following the $M$-vs-$T$ results, we heat treated sample 1 at 386 and 520 °C under flowing argon for 6 h. XRD results obtained after heat treatment at both temperatures showed that sample 1 followed the following reaction scheme:

$$1 \xrightarrow[\text{argon}]{386\,^\circ\text{C}} \underset{2}{Fe_3O_4} \xrightarrow[\text{argon}]{520\,^\circ\text{C}} \underset{3}{\alpha\text{-Fe(metallic iron pellet)}}.$$

At the lower temperature, sample 1 was oxidized to form $Fe_3O_4$ (probably by the cleavage of the oxygen from the carboxylate end of the oleic acid). At higher temperatures, the resultant magnetite was reduced (apparently by excess carbon) to $\alpha$-Fe (iron pellet), with a 10% weight loss. Both Curie points at 589 and 760 °C are in good agreement with the reported values for $Fe_3O_4$ and $\alpha$-Fe.[9]

The magnetization curve for sample 3 showed a very high room temperature saturation magnetization value of 200 emu/g, which is about 90% of the value for bulk iron.[9] The coercivity was constant at 20 Oe from 300 to 10 K. These results can be explained by small particle sintering ($1 \rightarrow 3$), along with removal of some carbonaceous material.

Sample 1 was fractionated by washing with pentane. In this way the larger particles (8–12 nm) remained on the frit (sample 4) while smaller ones (2–7 nm) were soluble and were obtained in the filtrate suspended in pentane.

Sample 4 was also amorphous according to XRD. The magnetization curve for 4 is shown in Fig. 2 and had a room-temperature magnetization of 54.9 emu/g, considerably higher than the value obtained for sample 1. The magnetic properties and physical appearance of sample 4 did not change over a 3-month exposure to air at room temperature. This remarkable air stability for a fine powder indicates that the oleic acid is very effective at protecting the particle surfaces. We also studied the temperature dependence of the coercivity. At 10 K the value was 700 Oe but leveled to 60 Oe at 300 K. From the TEM micrographs, we observed particles that were prolate spheroids (oblong, peanut shapes) with average dimensions of 12×8 nm. The VSM study of sample 4 showed a behavior similar to sample 1. Again, two Curie temperatures were detected which were in very good agreement with the reported values of $Fe_3O_4$ and $\alpha$-Fe.

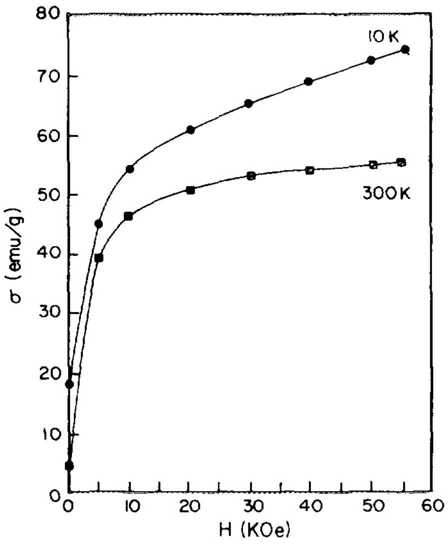

FIG. 2. Magnetization as a function of the applied field for sample 4.

Heat treatment of sample 4 at 520 °C under flowing argon produced a powder containing many metallic whiskers (sample 6). The saturation magnetization values for sample 6 were $M_s = 138.7$ emu/g (10 K) and 123.6 emu/g (300 K). similar to the conversion of $1 \rightarrow 3$, the conversion of $4 \rightarrow 6$ caused the coercivities to decrease to ~20 Oe. The XRD analysis showed that sample 6 consisted of mainly $\alpha$-Fe with some FeO.

## ACKNOWLEDGMENT

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