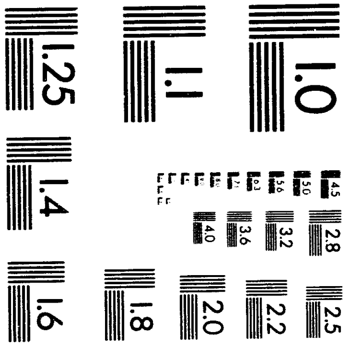
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MAGNETIC PROPERTIES OF NANOSIZE IRON CLUSTERS

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E. L. VENTURINI, J. P. WILCOXON and P. P. NEWCOMER
Sandia National Laboratories, MS 0345, Albuquerque, NM 87185-0345

ABSTRACT

Isolated, monodisperse α-Fe clusters between 1.4 and 15 nm in diameter were prepared inside inverse micelles using an oil-continuous, nonaqueous system. The magnetic properties of these clusters were studied in a SQUID magnetometer as a function of cluster size, temperature and applied magnetic field. The blocking temperature, coercive field and remanent moment of 12.5 nm Fe clusters in inverse micelles are significantly lower than those reported for clusters of similar α-Fe core size but with a surface oxide. The novel synthesis technique may yield metallic clusters with essentially intrinsic magnetic properties.

Preprint of paper submitted to Symposium V, 1994 Spring Meeting of Mat. Res. Soc., Page 1 of 6

INTRODUCTION

The properties of nm-sized magnetic particles have been studied both experimentally and theoretically for more than sixty years.[1-4] Interest in these materials has remained high because of their use in numerous practical applications in catalysis, magnetic recording, magnetic fluids and permanent magnets. In addition, there are fundamental research questions concerning the development of long-range magnetic order and associated hysteretic properties such as coercivity and remanence as the cluster size increases from a few atoms with all atoms at the surface to a large cluster with predominantly interior atoms.

Cluster synthesis and experimental handling play crucial roles in understanding the magnetic properties, particularly in separating the intrinsic properties from the effects of a surface layer [5-8] (such as a thin oxide shell) or particle-particle interactions due to agglomeration [8]. Here, we report initial studies on the magnetic properties of α-Fe clusters prepared by a novel synthesis technique which yields monodisperse particles and, we believe, mitigates both surface layer and agglomeration effects. Following are synthesis, microscopy and experimental details, presentation of the magnetic properties and concluding remarks placing our results in context.

EXPERIMENTAL DETAILS

Size-selected nanosize Fe clusters were grown by a process which is described in detail elsewhere.[9-11] Controlled nucleation and growth of metal clusters occurs in the interior of surfactant aggregates called inverse micelles. In our process an ionic salt (e.g., $FeCl_3$) is dissolved in the hydrophilic interior of the micelles while the surrounding continuous hydrophobic oil limits nucleation and growth to the micelle interior volume. We emphasize that the anhydrous salt is dissolved to form a transparent "ionic" solution but with a complete absence of water; in a sense the salt is "hydrated" by the micelle. The absence of water allows extremely novel and aggressive chemistry to be used in the reduction and growth process.[9,10] Encapsulation of the ionic salt solely in the micelle interior ensures spatial homogeneity during the nucleation process while the growth kinetics are determined by the rate of reduction of the metal salt and the diffusion of the micelles themselves (not the Fe atoms!). In this sense our synthetic method for size-selected clusters is fundamentally different than other cluster growth processes which occur in a continuous medium (e.g., gas or liquid phase growth) and which for fundamental reasons result in a power-law (i.e., log-normal) cluster size distribution.

MASTER

Three conditions can be used to control the final cluster size: the micelle size, intermicellar interactions (e.g., phase boundaries which determine micelle diffusion rates) and reaction chemistry. To provide a constant magnetic background independent of cluster size, we have employed a single type of surfactant and solvent and varied the reduction chemistry to control the final iron cluster size for the experiments described here. We varied the strength of the nonaqueous reducing agents used to reduce the Fe(III) to Fe(0) so that the most rapid reduction kinetics produced the smallest final iron clusters. Size-selected α-Fe metallic clusters with diameters between 1.4 and 15 nm were produced. Spectroscopy was used to demonstrate 100% reduction of the Fe(III) to the final Fe(0) cluster form.[11]

All reactions took place in anaerobic conditions in a Vacuum Atmospheres dry box with continuous oxygen and moisture removal and appropriate sensors. Typical oxygen levels were 0.1 to 1 ppm and moisture levels were 0.5 to 3 ppm in the dry box. All solvents and surfactants used were hplc grade and were completely dust free. The latter is critical to prevent inhomogeneous nucleation. Magnetization samples were weighed to determine total iron concentration and transferred to capped NMR tubes in the dry box to minimize oxygen exposure. The capped tubes were then removed from the dry box and transferred to the commercial SQUID magnetometer (Quantum Design MPMS) for magnetic characterization.

The inverse micelle system used in these experiments was DTAC (dodecyltrimethyl ammonium chloride) in hexadecane with hexanol used as a cosurfactant. Previous small-angle neutron scattering [9] has shown that this system provides stable growth in the cluster size range of 1 to ~18 nm which was well suited to the present investigation. After growth occurs, the resulting clusters are fully dispersed and stable in a variety of oils and their magnetic properties may be investigated as a function of cluster size. The stability against agglomeration is due to the presence of the surfactant on the cluster surface.

Fig. 1 is a bright field transmission electron micrograph (diffraction contrast) taken on a JEOL 1200EX at 120 kV showing the isolated, monodisperse 12.5±0.5 nm Fe particles formed in one synthesis (the scale is indicated by the 20 nm bar). Selected area electron diffraction confirmed that these particles are the bcc α-Fe phase. Other monodisperse Fe clusters produced by this surfactant/solvent process ranged from 1.4±0.1 to 15.0±0.5 nm, all below the maximum size of 16.4 nm [12] for single magnetic domain Fe.

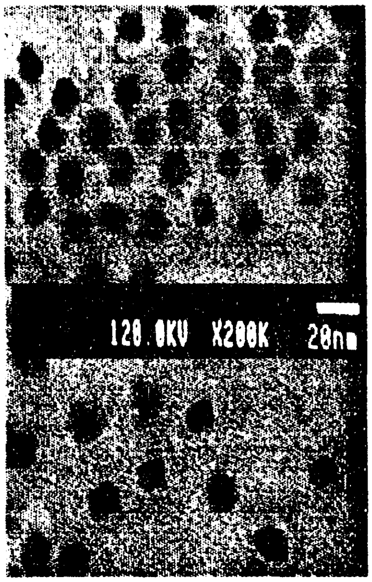

Fig. 1. TEM photograph showing monodisperse, 12.5±0.5 nm Fe clusters.

MAGNETIC MEASUREMENTS

Fig. 2 compares the response to an applied magnetic field at 5 K for the dissolved $FeCl_3$ salt (Fe^{+3} ions in a frozen solution) before adding the reducing agent (open triangles) to that of 12.5 nm Fe clusters after reduction (solid triangles). The dashed line is a Brillouin function fit to the Fe^{+3} ion data using a g-factor of 2 and an angular momentum of 2.5. The agreement confirms the presence of isolated Fe^{+3}; further, the low-field slope (susceptibility) decreases by a factor of 2 between 5 and 10 K, suggesting negligible magnetic interactions between the ions. In contrast, the Fe clusters show a distinct saturation in their response for fields above 1 tesla, consistent with ferromagnetic or superparamagnetic behavior characteristic of strong magnetic interactions within the clusters. Note the qualitative difference between the isolated ions and the clusters: the isolated Fe^{+3} ions exhibit a linear response to applied field at low fields and a nonlinear response at high fields while the 3.7 nm Fe clusters show a nonlinear response (and a larger moment per gram) at low fields but saturate to a constant moment in moderate fields.

Fig. 3 shows isothermal hysteresis data (moment M versus applied magnetic field H) measured at 5 K following zero-field cooling. The open circles denote the initial response to an increasing field, the solid triangles for a decreasing field, and the open triangles for an increasing field. The data are shown between -0.25 and +0.25 tesla, but the actual hysteresis measurement used field strengths to ±2 tesla. These 12.5 nm α-Fe clusters are ferromagnetic at 5 K with the data approaching saturation and exhibiting reversibility at high field strengths. There is a substantial remanent moment M_{rem} at zero field and a moderate coercive field H_{coer} (where the moment crosses through zero following saturation). The saturation moment for these particles at 5 K, determined by plotting M versus 1/H and extrapolating to infinite field, is 2.2×10^{-3} emu or ≈25 emu/g for the 88 μg of Fe in this sample; the saturation moment for bulk α-Fe is 220 emu/g at low temperatures [12]. The total diamagnetic (negative) signal from the surfactant, solvent, glass NMR tube and reducing agent salts (measured in a separate experiment) is linear in applied field and -6.8×10^{-4} emu in 1 tesla at 5 K; all data have been corrected for this diamagnetism. Although this correction is small at the fields strengths in Fig. 3, it is large at 5 tesla for the dilute Fe samples studied here. Since the Fe sample plus surfactant/solvent/reducing agent is measured independently from the diamagnetic correction, there is considerable uncertainty in the determination of a saturation value by plotting the corrected moment versus 1/H due to the dominance of the correction term.

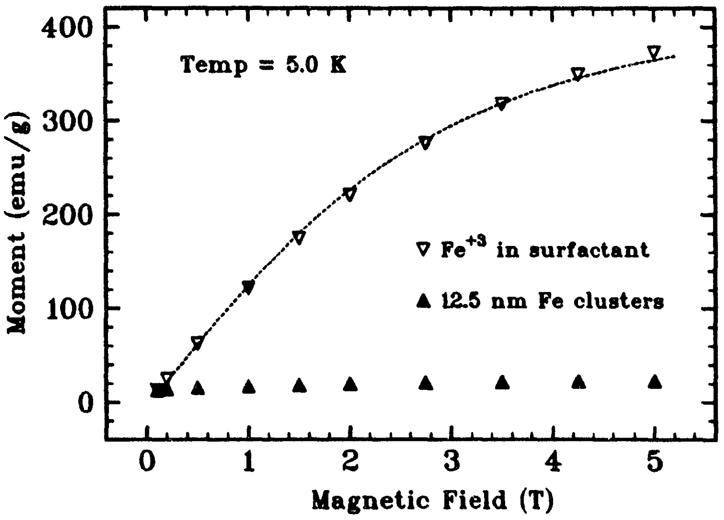

Fig. 2. Moment versus field at 5 K before and after reduction to Fe clusters.

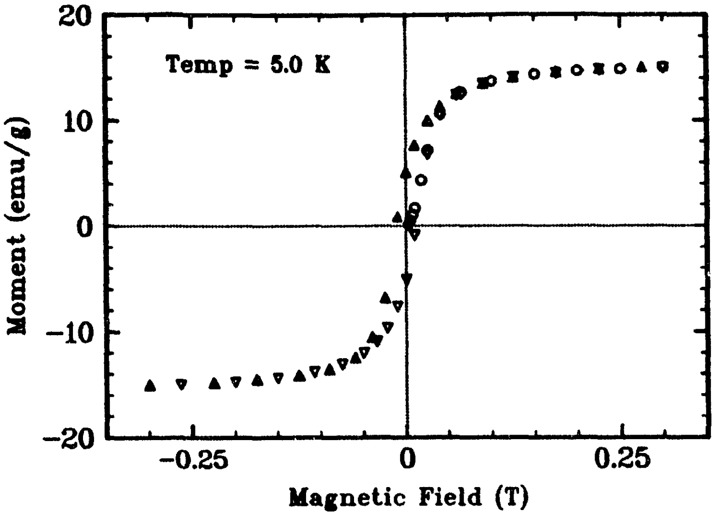

Fig. 3. Hysteresis at 5 K for 12.5 nm α-Fe clusters.

The magnetic moment of each Fe particle in a frozen solution will exhibit random rotations driven by thermal fluctuations.[13] Opposing these fluctuations is the magnetic anisotropy energy $E_{anis} = KV$ where K is the anisotropy energy per unit volume and V is the volume of the particle. An assembly of such particles will relax to equilibrium through thermal fluctuations on a time scale τ given by

$$\tau = \tau_0 \exp[KV/kT] \qquad (1)$$

where τ_0 is a characteristic time on the order of 10^{-9} seconds, k is the Boltzmann constant and T the absolute temperature.[14]

One of the distinguishing features of small, single domain magnetic particles is the appearance of a blocking temperature T_B defined as the temperature where the relaxation time τ in Eq. (1) becomes comparable to the experimental time of 100 seconds. For temperatures above T_B, the magnetization versus applied magnetic field is reversible due to thermal fluctuations, i.e., the sample exhibits no remanence or coercivity in a hysteresis measurement.[14] Fe has cubic anisotropy with an anisotropy energy K_{Fe} of 4.6×10^5 ergs/cm^3; the easy direction for magnetization is one of the [100] axes. For spherical Fe particles with cubic anisotropy, the K in Eq. (1) must be replaced by K/4.[14] Using Eq. (1) for the 12.5 nm Fe particles and $\tau_0 = 10^{-9}$ seconds, we predict $T_B \approx 34$ K for a thermal relaxation time of 100 seconds (the calculated relaxation time is 3×10^9 sec at 20 K and 18 nsec at room temperature).

An experimental blocking temperature can be determined from isothermal hysteresis measurements using the vanishing of remanence and coercivity. Fig. 4 shows the remanent moment and coercivity versus temperature for the 12.5 nm particles; both vanish between 50 and 60 K. This experimental T_B is only 50% higher than the calculated value and the latter is extremely sensitive to particle size and morphology. For example, 14 nm particles have a predicted T_B of 47 K which would agree with our experimental result. In addition, various improvements to Eq. (1) have been suggested.[15] We have also studied a sample with 3.7 nm α-Fe particles and found an experimental T_B of 15 K. The volume of these particles is only 2.6% of that for the 12.5 nm clusters, and Eq. (1) predicts a blocking temperature of 0.9 K. The cause of this large disagreement between simple theory and experiment for these 3.7 nm clusters is not understood. It may be that the assumptions of spherical particles and bulk magnetic anisotropy are not valid for very small cluster sizes.

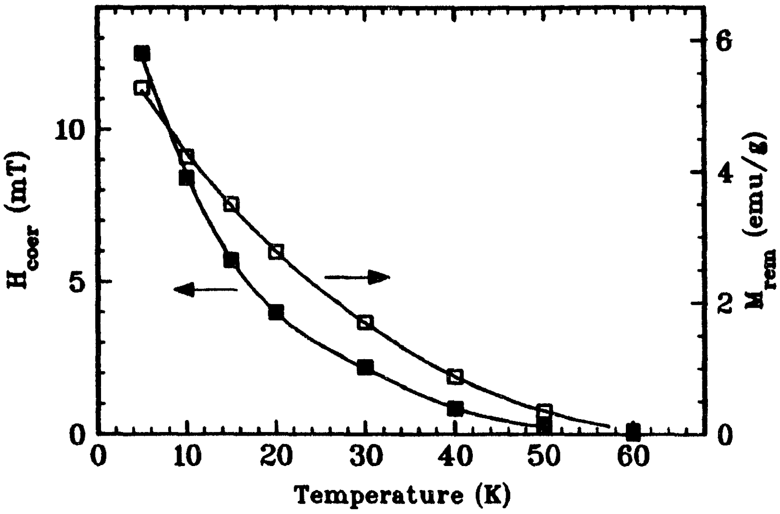

Fig. 4. Coercive field and remanent moment versus temperature for 12.5 nm α-Fe clusters.

DISCUSSION AND CONCLUSIONS

Nanometer-sized particles of Fe, Co or Ni are promising for applications requiring a high saturation magnetization and large coercivity. We have developed a novel synthetic procedure for size-selected clusters between 1 and ~18 nm in diameter. The nonaqueous synthesis under anaerobic conditions produces clusters which are individually isolated within inverse micelles and thus stabilized against agglomeration. Careful sample handling permits studies with minimal exposure to oxygen or moisture. Magnetic data for the saturation magnetization M_{sat}, remanent moment M_{rem}, coercivity H_{coer} and superparamagnetic blocking temperature T_B of a sample with 12.5 ± 0.5 nm α-Fe clusters differ considerably from literature values.

M_{sat} is ≈25 emu/g at 5 K from extrapolation of magnetization versus 1/H or roughly 10% of the 220 emu/g for bulk α-Fe. Literature values range from 20% of bulk Fe for ~10 nm particles [5,8] to the bulk value for Fe clusters with 500 to 700 atoms [16] (~2.5 nm diameter). However, the 10 nm particles were oxidized [5,8] and the effects of an oxide shell on the measured M_{sat} of the α-Fe core are not clear. M_{rem} is ≈5 emu/g at 5 K and vanishes between 50 and 60 K for the 12.5 nm Fe clusters in inverse micelles compared to 30 emu/g at both 220 and 300 K for oxidized Fe particles with a 3.3 nm diameter metallic core [5]. Again, oxidation of the Fe clusters appears to drastically alter the superparamagnetic transition and remanence.

Coercivity varies strongly with particle size, reaching a maximum for ~15 nm particles of Fe and Co.[17] However, the origin of the coercivity is poorly understood, particularly the effect of surface oxide. The maximum calculated H_{coer} for single domain Fe particles is 50 mT due to magnetic anisotropy while measured values are twice as large.[17] Oxidized α-Fe can have H_{coer} up to 340 mT at 10 K for 6 nm particles [5] and 160 mT for 13 nm particles [6]. The latter is a factor of 20 larger than $H_{coer} \approx 8$ mT at 10 K for the 12.5 nm α-Fe particles studied here (Fig. 4). More importantly, oxidized Fe particles with α-Fe core diameters between 8.4 and 14 nm exhibited strong coercivities of 40 to 110 mT at room temperature [5], while the coercivity of our 12.5 nm α-Fe particles decreases rapidly with increasing temperature and vanishes between 50 and 60 K, i.e., at T_B (Fig. 4). In one experiment, Fe particles between 6 and 22.7 nm in diameter were synthesized by gas evaporation, collected on a Ag film and covered by a second Ag film inside the evaporation chamber to minimize oxidation.[5] These samples exhibited large, nearly temperature-independent H_{coer} [5], strikingly different from the behavior of the present Fe clusters.

Superparamagnetic blocking temperatures were 50-60 K for 12.5 nm clusters and 15 K for 3.7 nm clusters in inverse micelles. The former value agrees reasonably well with the calculated T_B based on cluster size and the magnetic anisotropy of bulk Fe while the latter value is considerably above the calculated T_B. Reported values ranged from 230 K for 5.3 nm Fe cores to 120 K for 2.5 nm cores of oxidized clusters.[5] Granular films with 3 to 9 nm α-Fe particles in a BN host matrix had a field-dependent blocking temperature between 35 and 40 K.[7] However, particle interactions were evident in the strong dependence of coercivity on Fe concentration [7] and these interactions may affect the measured T_B.

Our novel synthesis technique for isolated, size-selected α-Fe clusters in the 1 to 18 nm range provides an opportunity to test various predictions for coercivity, remanence and saturation magnetization as a function of particle size and temperature. The same synthesis has been used for preparing size-selected Co and Ni clusters. The magnetic behavior of these particles should identify the separate roles of thermal energy, magnetic anisotropy and surface versus "bulk" atoms as the cluster size approaches a few unit cells, thus improving our understanding of magnetic phenomena in this size range.

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