SIZE AND INTERFACE DEPENDENT MAGNETIC PROPERTIES OF ENCAPSULATED METAL CLUSTERS

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1. Introduction

The properties of magnetic nanoparticles is an area of current active interest with many problems of fundamental importance [1-4]. The nanoscale places particles at the single domain size where the coercivity can have a maximum or below this size where the particles eventually become superparamagnetic with no coercivity [5]. The density of states of various excitations in nanoparticles is affected by size through coarsening and/or introduction of a finite wavelength cut off. And, perhaps most importantly, nanoparticles have a large fraction of surface atoms which may have properties distinctly different than those in the bulk. Moreover, the exposed nature of the surface makes it susceptible to interfacial materials which might modify the properties of the surface atoms.

In this paper we study surface/interfacial effects on the magnetic properties of core/shell nanoparticles. The core materials are either Fe, Co, and Ni and the shell materials are either Mg or MgF_2. This variety allows us to distinguish interfacial effects from size effects. Our synthetic method allows us to vary the core size so that we can study size effects as well.

2. Experimental Procedures

Ultrafine particles of [Mg]Fe and [MgF_2]Fe, [MgF_2]Co, and [MgF_2]Ni were prepared by the Solvated-Metal-Atom-Dispersion (SMAD) method [6]. As shown in figure 1, vapors of the two components (Mg and Fe or MgF_2 and Fe, Co, or Ni) were vaporized from two electrically heated sources in a vacuum chamber, and these vapors codeposited simultaneously at 77 K with the vapor of a large molar ratio excess of a matrix diluent, usually pentane. Molar ratios of evaporated material were: for Mg:Fe, 7:4 and 8:1; for MgF_2:Fe, 2:1 and 8:1; for MgF_2:Co, 2:1; and for MgF_2:Ni, 2:1.

I. Nedkov and M. Ausloos (eds.), Nano-Crystalline and Thin Film Magnetic Oxides, 159–164.

After the deposition of about 1.0 g of the metal/metal or metal/metal fluoride with 80-100 ml of pentane, the frozen matrix was allowed to warm up to room temperature. The pentane was removed under vacuum and a free flowing powder of the Mg-Fe or MgF_2-Fe (Co, Ni) as an intimate mixture was obtained. Subsequent heat treatments in the range 150 to 700°C were performed under Ar to cause controlled phase segregation to a core-shell morphology where the transition metal is the core within each particle. Characterization of samples employed X-ray powder diffraction (XRD), Transmission Electron Microscopy (TEM), elemental analyses, and SQUID magnetometry.

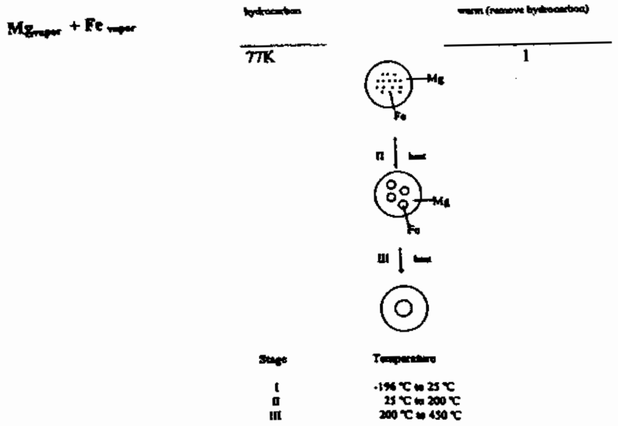


Figure 1. Schematic of the nano-particle synthesis scheme by the SMAD method.

3. Results and Discussion

3.1 MAGNETIC ANISOTROPY

The low field (H = 200 Oe) magnetization curves for as-prepared [Mg]Fe particles with evaporated Mg:Fe molar ratios of 7:4 and 8:1 and [MgF_2]Fe with 8:1 molar ratio are given in Figure 2. Blocking temperatures of 70 K, 25 K and 10 K are found, respectively. X-ray powder diffraction using the Scherrer formula gave an average Fe crystallite diameter of about 3 nm for each system. The Fe crystallites in these particles were roughly spherical, so they can be considered as uniaxial clusters. According to the Neel-Arrhenius Law, the blocking temperature T_B and the magnetic anisotropy constant K are related by [5]

$$25\, k\, T_B = KV. \qquad (1)$$

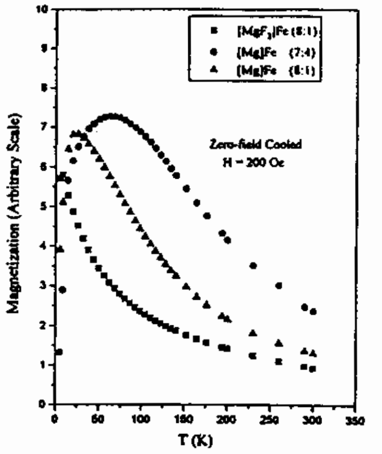


Figure 2. Temperature-dependent magnetization of as-prepared [Mg]Fe particles with Mg:Fe molar ratios of 7:4 and [MgF$_2$]Fe with molar ratio 8:1.

V is the particle volume, and k is Boltzmann's constant. Thus using the measured blocking temperatures and a particle diameter of 3 nm the effective anisotropy constants can be calculated to be K= 1.7 x 10^7, 6x10^6 and 2.4 x 10^6 erg/cm^3, respectively. These can be compared to the anisotropy constant of single crystal bulk iron, which is 4.8 x 10^5 erg/cm^3 at room temperature and 5.8 x 10^5 erg/cm^3 at 70K [5], so the encapsulated 3nm iron crystallites have an anisotropy constant at least one order of magnitude higher than that of the bulk. It is very interesting to note that although the Fe particle size is about 3nm for all the samples, their anisotropy constants are far different from one another. Comparing the Mg:Fe = 8:1 and 7:4 systems it is reasonable to conclude that strong interparticle, dipolar interactions must increase K at high Fe concentration. Comparing the Mg:Fe = 8:1 system and the MgF$_2$:Fe = 8:1 systems, we find that Fe particles encapsulated in magnesium have higher anisotropy energy than Fe particles encapsulated in MgF$_2$. This may be due to a different interfacial interaction or a stronger cluster-cluster interaction in Mg than in MgF$_2$ despite the essentially same interparticle separation. The coercivity H$_c$ was measured for the [Mg]Fe system as a function of the Fe core size and temperature. The results, shown in figure 3, are typical for fine particles and imply a single domain size of about 18 nm, the peak in H$_c$ vs. size. This is in good agreement with previous measurements.

3.2. MAGNETIZATION

The saturation magnetization was measured using 1/H →O extrapolation with H< 55Oe. Figures 4-7display Ms vs. T for the [Mg]Fe, [MgF$_2$]Fe, [MgF$_2$]Co, and [MgF$_2$]Ni systems, respectively.

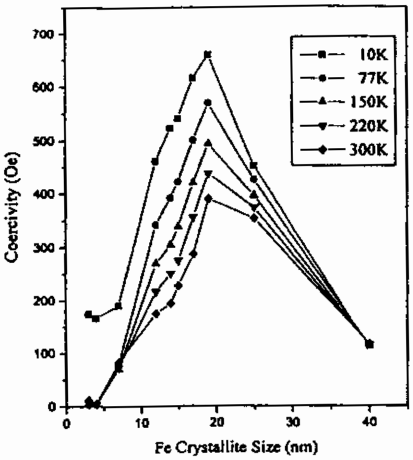


Figure 3. Size dependence of coercivities of as-prepared [Mg]Fe particles with an Mg: Fe molar ratio of 7:4.

Three notable features could be discerned from the graphs:

1. A strong temperature dependence develops with decreasing size.
2. The temperature dependence depends on the interface; compare the [Mg]Fe and $[MgF_2]Fe$ systems.
3. At T→0K, the magnetization is quenched, more so with declining size, in the order Ni > Co > Fe

We have fit Bloch's Law [5] to the data for [Mg]Fe and $[MgF_2]Fe$

$$M_S(T) = M_S(0)\,(1 - BT^b). \tag{2}$$

Results are given in Table I. We find the Bloch exponents show a significant decrease from the bulk value of b=3/2 found in larger sizes while the Bloch constant increases by orders of magnitude as the size declines. Moreover, slightly different dependencies are found for the two different interfaces.

The T=0K quench of the magnetization, especially apparent in the Co and Ni systems, has a rough inverse diameter dependence to imply the quench of the magnetization is proportional to the specific interfacial surface area. This further implies that the quench is due to the shell material's influence on the transition metal core, and the influenced region has a thickness independent of the particle diameter.

These quenching data can be explained with a simple model in which electrons are inserted from the shell material into a constant thickness surface layer of the transition metal core. Note that in our model the chemically homogeneous transition metal core takes on a magnetically inhomogeneous, core-shell morphology, a partially quenched shell of constant thickness and an unquenched core. We assume that the quenched shell for each transition metal results from the same electron density

Figure 4 Saturation magnetization normalized by the bulk saturation magnetization plotted against temperature for [Mg]Fe particles with different Fe crystallite sizes.

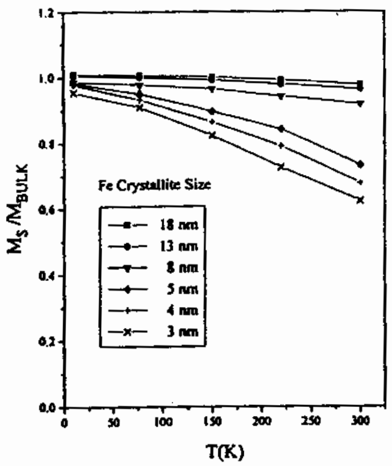


Figure 5 Saturation magnetization normalized by the bulk saturation magnetization plotted against temperature for [MgF$_2$]Fe particles with different Fe crystallite sizes.

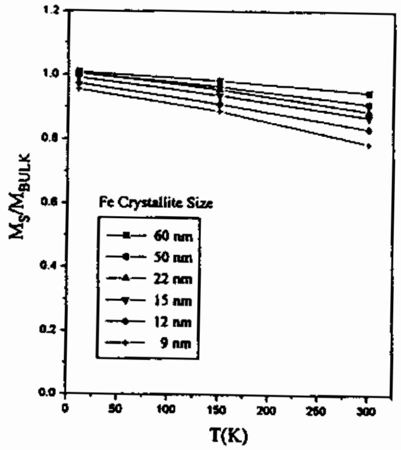


Figure 6 Saturation magnetization normalized by the saturation magnetization plotted against temperature for [MgF$_2$]Co particles with different Co crystallite sizes.

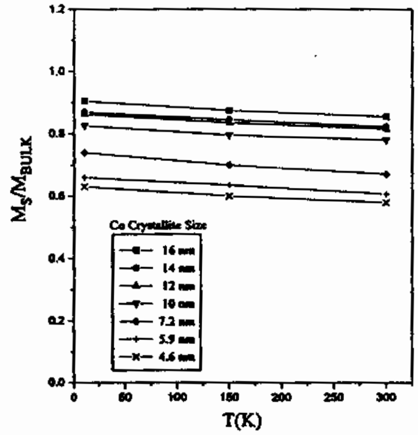
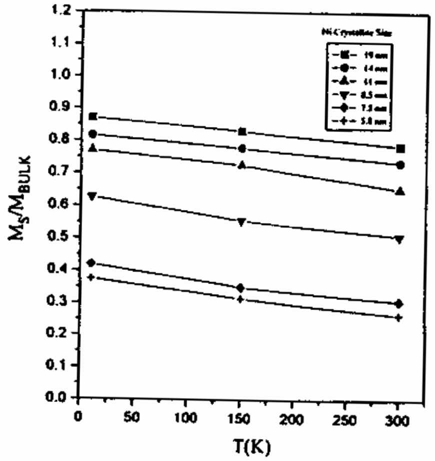


Figure 7 Saturation magnetization by the bulk saturation magnetization plotted against temperature for [MgF$_2$]Ni particles with different Ni crystallite sizes.



added to the d-bands of the metals. This assumption is physically reasonable since the order of quenching, Ni>Co>Fe, is the inverse of the order of the electron vacancies in the minority, up-spin part of the d-band 0.6, 1.7 and 2.2 electrons per atom, respectively, which is responsible for the magnetic moment of the metal. Thus, for example, if 0.5 electrons per atom is added to each metal, the fractional quench for the surface layer is 83%, 31%, and 23% for Ni, Co and Fe, respectively, which qualitatively explains the order of quench.

Table 1. Variation in Bloch constant and Bloch exponent for Fe crystallites of different sizes encapsulated in Mg metal or MgF_2.

[Mg]Fe

Fe core diam (nm)	b	B
3	1.12	$7x10^{-4}$
3	1.27	$3x10^{-4}$
3.5	1.35	$1.7x10^{-4}$
4	1.28	$2.2x10^{-4}$
5	1.39	$1.4x10^{-4}$
6	1.61	$2.8x10^{-5}$
8	1.33	$1.4x10^{-5}$
13	1.45	$8.7x10^{-6}$
13	1.46	$9.5x10^{-6}$
18	1.63	$3.3x10^{-6}$
18	1.59	$5.6x10^{-6}$
10	1.5	$2.9x10^{-5}$

[MgF_2]Fe

Fe core dia.	b	B
3	0.37	$5x10^{-2}$
4	0.83	$2.x10^{-3}$
6	1.55	$2.4x10^{-5}$
5	1.31	$1.1x10^{-4}$
7.5	1.51	$3.5x10^{-5}$

4. Summary

The magnetic properties of completely oxygen-free [Mg]Fe, [MgF_2]Fe, [MgF_2]Co, and [MgF_2]Ni core/shell particles were studied. An interface dependent enhanced anisotropy energy was observed in the 3 nm Fe crystallite materials. The magnetic coercivities of these oxygen-free metal particles were generally much lower than the coercivities of oxide-coated particles. The saturation magnetization values of the encapsulated Fe, Co and Ni particles were found to be size, interface, and temperature-dependent. The temperature dependence obeyed Bloch's Law, but with parameters that deviated from bulk values with decreasing size dependent on the interfacial material..

5. References

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