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ENCAPSULATED IRON, COBALT AND NICKEL NANOCRYSTALS; EFFECT OF COATING MATERIAL (Mg, MgF_2) ON MAGNETIC PROPERTIES

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Abstract- *Nanometer sized core/shell particles of [Mg]Fe, [MgF_2]Fe, Co, and Ni, where Mg or MgF_2 are the shell materials, have been prepared by a low temperature matrix method. Phase segregation was accomplished within each individual particle by controlled heating to yield the completely oxide free core/shell particles, which were sealed in glass or quartz tubes and studied by SQUID magnetometry. For [Mg]Fe samples with very small Fe crystallites, enhanced anisotropy energies were observed. For core/shell particles, saturation magnetization [Ms] values for Fe, Co, and Ni were found to be both size and temperature dependent. Indeed, M(T) behavior is richly dependent on size in the nanometer range, and on the type of surface interface. Quantitative assessment and discussion of Bloch exponent and Bloch constant variations as iron crystallite size change are discussed.*

INTRODUCTION

The chemistry and physics of nanoscale magnetic particles has been and continues to be an area of great interest [1-4]. From a fundamental perspective the study of nanoparticles sheds light on how bulk properties transform to atomic as size decreases. When nanoscale, the fraction of surface material becomes dominant, hence bulk properties may either give way to surface properties and/or be significantly perturbed by the surface. Moreover, the large surface fraction opens the opportunity for manipulation of properties via interfacial interactions.

In this paper we present experimental data for the magnetization temperature dependence of nanoscale iron particles. Our synthetic technique [5-7] has allowed us to systematically vary the iron particle size. Furthermore, our particles are interfaced with two different materials, hence we study the important interfacial interaction as well. In general for temperatures well below the Curie temperature, the magnetization ~~temperature dependence~~ arises due to spin wave fluctuations as first described by Bloch who found [8]

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

In Eq.(1), M(T) is the temperature dependent magnetization, B is the Bloch constant and b is the Bloch exponent. The exponent is given by b = 3/2 for a three dimensional system and has been well verified [8].

The first "non-bulk" theoretical studies of spin waves and M(T) were carried out by Mills and Maradudin [9-11] using calculations and Wildpaner and coworkers [12,13] using simulations. Mills and Maradudin considered surfaces and found the Bloch exponent remained b =3/2 as in the bulk, and $B_{surf} = 2B_{bulk}$. The simulations considered particles of various sizes and found stronger temperature dependencies with decreasing size but did not fit the results to Eq. (1). Furthermore, the spin excitations were not homogenous throughout the particle. More recently, Hendriksen et al.[14] considered the spin wave spectrum of particles by solving the Heisenberg Hamiltonian. Again the excitations were a function of radial position in the particles, and the overall result was a prediction that the exponent b should increase above the bulk value of 3/2 inversely proportional to the particle size.

Experimental investigations of M(T) for nanoparticles yield a mixed story. Pierce et al. [15] studied the magnetization of macroscopic surfaces and found results consistent with Mills and Maradudin. Linderoth et al. [16] followed up their calculations [14] with measurement on Fe-C particles with a diameter of 3.1 nm and found b = 1.9 in qualitative agreement with their theory. Xiao and Chen [17] looked at iron embedded in SiO_2 at ~ 50% volume fraction. The particle size was 2-3 nm. They found b = 3/2 with $B_s \simeq 10B_b$. In previous work involving $MnFe_2O_4$ particles [18], we found b in the range 1.5 to 1.9 for sizes in the range 5 nm to 15 nm. Thus no coherent story is told by the few experiments available, and there is no adequate match with theory.

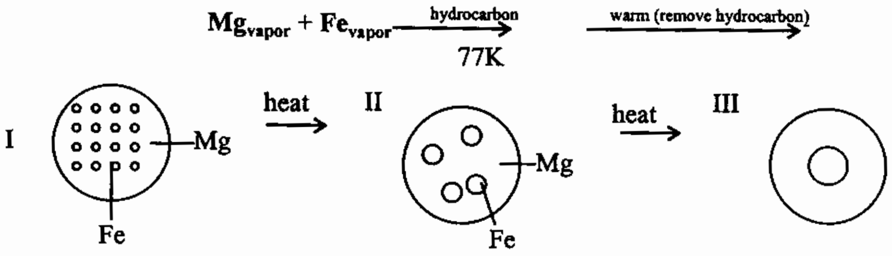
RESULTS

The core/shell particles were prepared by the Solvated Metal Atom Dispersion (SMAD) method, which involves codeposition of vapors of metal and shell material (Mg or MgF_2) with excess hydrocarbon, followed by warming and heat treatments, see Fig. 1 [6,7].

X-ray diffraction measurements showed the characteristic diffraction pattern of α–Fe for both the as prepared and annealed samples. No evidence for oxides of iron was seen corroborating the air stability of the iron cores of the samples. The breadth of the primary diffraction line of iron near $2\theta = 45^\circ$ was used with the Scherrer formula [19] to estimate the iron crystallite size. Transmission electron microscopy showed roughly spherical iron particles immersed in a matrix which was Mg and MgO for the [Mg]Fe samples or MgF_2 for the [MgF_2]Fe samples.

The SQUID magnetometer was used for magnetic measurements. The saturation magnetization was determined by $H^{-1} \rightarrow 0$ extrapolation using fields of $\underline{H} \leq \underline{.55T}$. Results are shown in Figs. 2 and 3. Figure 3 shows a significant magnetization quench for the [MgF_2]Fe samples, more so for smaller particles. We believe this quench is due to an electron donation from the MgF_2 coating into the unfilled minority d-band of the iron, and a more detailed discussion of this effect will be given in another paper. Regardless of this quench (or lack of it in the [Mg]Fe samples) Figs. 2 and 3 both show increasing temperatures dependencies of Ms with decreasing particle size. In fact, the concave upward dependence of

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



Stage	Temperature
I	-196°C to 25 °C
II	25 °C to 200 °C
III	200 °C to 450 °C

Figure 2. Temperature dependence of magnetization of [Mg]Fe Particles

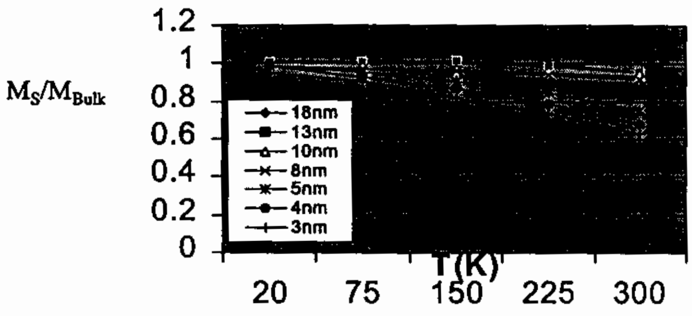
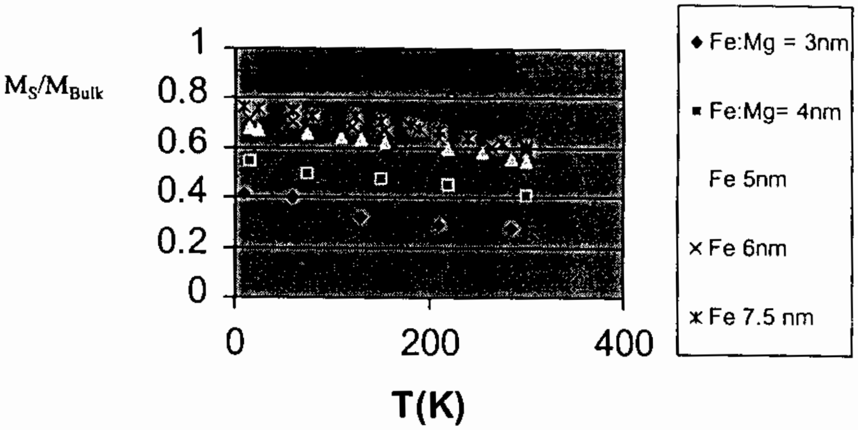


Figure 3. Temperature dependence of magnetization of [MgF_2]Fe Particles



Ms vs. T in Fig. 3 for the dia. = 3nm [MgF_2]Fe sample indicates a Bloch exponent $b<1$. It is these qualitative observations that represent the main result of this paper, and which we now quantify.

The form of Bloch's Law, Eq.(1), implies that the magnetization depression M(0)-M(T) is a power law with T. Thus a double logarithmic graph of these quantities will yield straight lines, if Bloch's law holds, the slopes of which are the Bloch exponent b and with intercepts related to BM(0). The observed data all fall on the lines to imply Bloch's law holds for our nanoparticles. Again, qualitative comparison of the figures for the two samples shows differences implying that interface as well as size (and magnetic material) is important in determining the M(T) behavior.

Linear fits of Eq.(1) to the data yield the Bloch parameters b and B. Both data sets (for Mg and MgF_2 shell materials) approach the known bulk value for iron as size increases. For all but our largest particles (18 nm) the Bloch constant is significantly greater than the bulk values, increasing by as much as two orders of magnitude. Considering Bloch constants for the two smallest sizes, 3 and 4 nm, for the [MgF_2]Fe system, these sizes yield Bloch constants of $B(3\text{ nm}) = 5\times10^{-2}$ and $B(4\text{nm})= 2\times10^{-3}$, which are significantly greater than for the corresponding sizes in the [Mg]Fe system.

DISCUSSION AND CONCLUSION

Our results may be summarized as follows: 1)nanoscale particles obey the form of

Bloch's law as written in Eq.(1). 2). With the decreasing size, the Bloch exponent falls from the bulk value of b =3/2 to smaller values. 3) With decreasing size the Bloch constant rises from the bulk values by orders of magnitude. 4) The chemistry of the interface is important in determining the size dependent properties of M(T).

We reviewed previous work on the behavior of M(T) for reduced dimension systems in the Introduction. The qualitative theoretical expectation is that the reduced coordination at the surface will cause the spins at the surface to be more susceptible to thermal excitation which leads to larger magnetization temperature dependencies. This qualitative expectation is borne out by our data. Since reduced coordination is a factor, it follows that the nature of the coordination is also important, and this is also supported by the fact that the [Mg]Fe and [MgF_2]Fe systems show different dependencies of the Bloch parameters with size. Beyond these qualitative comparisons, no quantitative agreement can be made either with theory or past experiment. However, we can conclude that MgF_2 donates electron density to the core Fe crystallite more intensely than Mg. This may be due to a ligand effect where fluoride strongly binds and donates to the iron d-orbital system.

In conclusion it appears that M(T) behavior is richly dependent on size in the nanometer range, and on the type of interface. Despite this complexity, the form of Bloch's law continues to hold. Future work to unravel these dependencies must systematically vary all three parameters.

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