Magnetization temperature dependence in iron nanoparticles

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The temperature dependence of the saturation magnetization of iron nanoparticles protected from oxidation by a shell of either magnesium or magnesium fluoride is reported. For iron crystallite sizes ranging from 3 to 18 nm, Bloch's law is found to hold, but with nonbulk parameters dependent on both size and interface. The Bloch exponent decreases from the bulk value with decreasing size while the Bloch constant increases from the bulk value orders of magnitude with decreasing size. These size dependencies are different for the Mg and MgF_2 coated samples to imply important interfacial effects. [S0163-1829(98)04845-0]

I. INTRODUCTION

The physics of nanoscale magnetic particles is an area of enduring 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. Knowledge of these fundamental properties is essential for creative use of nanoparticles in important technical applications such as data storage, magnetic refrigeration, and ferrofluids.

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 ''nonbulk'' theoretical studies of spin waves and $M(T)$ was carried out by Mills and Maradudin[9–11] using calculation and Wildpaner and co-workers[12,13] using simulations. Mills and Maradudin considered surfaces and found the Bloch exponent remained $b = 3/2$, as in the bulk, but the Bloch constant of the surface was predicted to be twice that of the bulk, $B_{surf} = 2B_{bulk}$. 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 found to be inhomogeneous throughout the particle. More recently,

Hendriksen, Linderoth, and Lindgard[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 $\frac{3}{2}$ 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 a 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 Chien[17] looked at iron imbedded in SiO_2 at ~50% volume fraction. The particle size was 2–3 nm. They found $b = \frac{3}{2}$ with $B_{surf} \simeq 10B_{bulk}$. In previous work involving $MnFe_2O_4$ particles,[18] we found b in the range 1.5–1.9 for sizes in the range 5–15 nm. Thus no coherent story is told by the few experiments available, and there is no adequate match with theory.

II. EXPERIMENTAL PROCEDURES

Ultrafine particles of [Mg]Fe and [MgF_2]Fe were prepared by the solvated-metal-atom-dispersion (SMAD) method.[5–7] In each case the iron particles were coated with the Mg or MgF_2, hence we use the notation [shell] core. Briefly, vapors of the two components (Mg or MgF_2 and Fe) 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; and for MgF_2:Fe, 2:1 and 8:1. 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 as an intimate mixture was obtained. Subsequent heat treatments were performed as desired to cause controlled phase segregation to a core-shell morphology where the transition metal is the core within each particle. In this work exposure to oxygen was
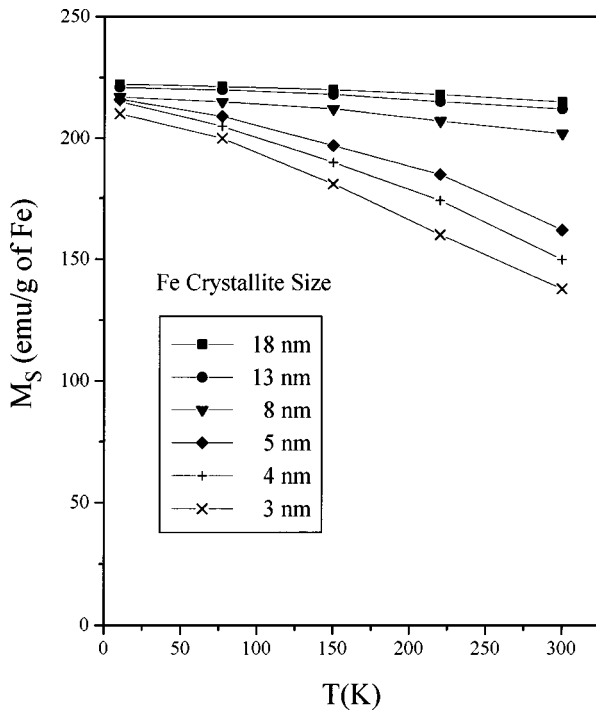
FIG. 1. Saturation magnetization versus temperature for different size iron crystallites in the [Mg]Fe system.

FIG. 2. Saturation magnetization versus temperature for different size iron crystallites in the [MgF_2]Fe system.

precluded by sealing the sample in a quartz tube sample holder and subsequent heat treatments and magnetic measurements carried out without removal from the sample holder. Before sealing, a piece of Mo or Al foil was pressed onto the top of the samples to hold the particles in place for magnetic measurements. X-ray diffraction studies were carried out on mineral oil protected particles. Heat treatments to anneal the samples were carried out under Ar at temperatures of 150–700 °C. Annealing increased the iron crystallite size and thus allowed control of this important parameter. Detailed characterization of samples has been described previously.[6,7]

III. RESULTS

X-ray diffraction measurements showed the characteristic diffraction pattern of α-Fe for both the prepared and annealed samples with no evidence for the oxides of iron. The breadth of the primary diffraction line of iron near $2\theta = 45°$ was used with the Scherrer formula[19] to determine the iron core crystallite size. Transmission electron microscopy showed roughly spherical iron particles immersed in a matrix that 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 M_s was determined by $H^{-1} \to 0$ extrapolation using fields of $H \le 55$ KOe. Results are shown in Figs. 1 and 2. Figure 2 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). Figures 1 and 2
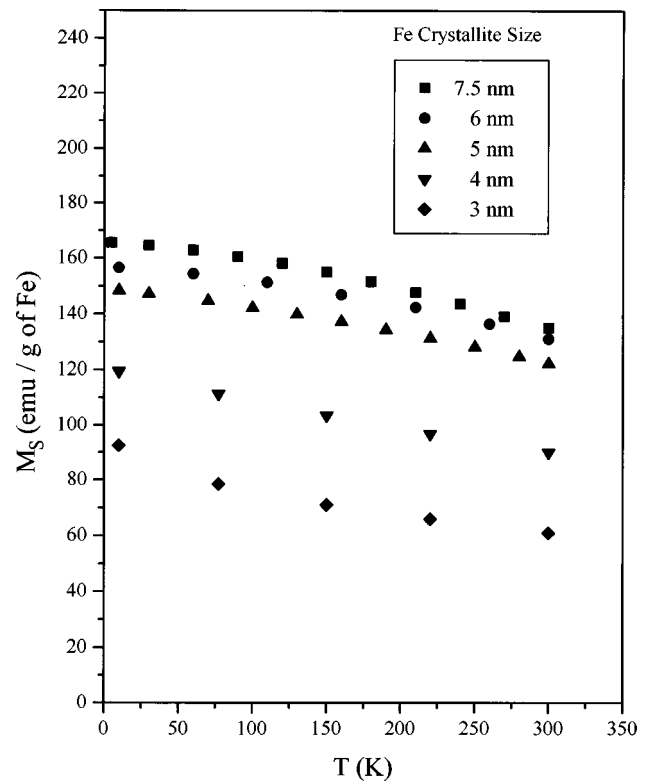

FIG. 3. Saturation magnetization depression relative to its value as $T = 0$ K versus temperature for different size iron crystallites in the [Mg]Fe system.
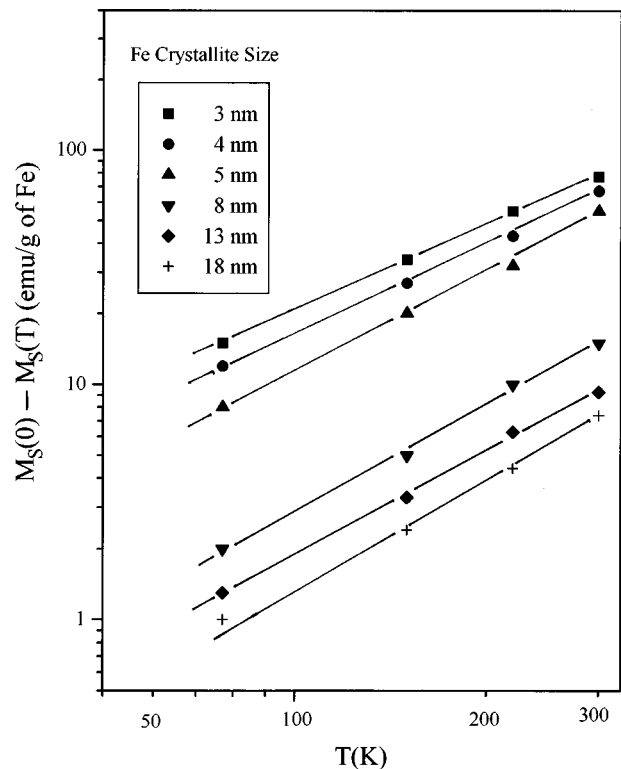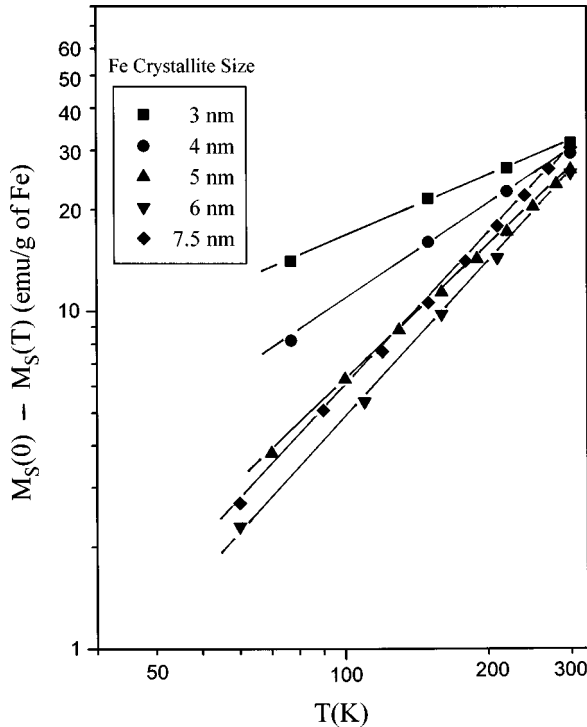
FIG. 4. Saturation magnetization depression relative to its value as $T = 0$ K versus temperature for different size iron crystallites in the [MgF$_2$]Fe system.

both show increasing temperatures dependencies of M_s with decreasing particle size. In fact, the concave upward dependence of M_s vs T in Fig. 2 for the diam=3 nm [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 $M_s(0) - M_s(T)$ is a power law with T. Thus, if Bloch's law holds, a double logarithmic graph of these quantities will yield straight lines the slopes of which are the Bloch exponent b and with intercepts related to $BM_s(0)$. Such graphs are shown in Figs. 3 and 4 for [Mg]Fe and [MgF$_2$]Fe, respectively. The data all fall on lines to imply that 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 $M_s(T)$ behavior.

Linear fits of Eq. (1) to the data as plotted in Figs. 3 and 4 yield the Bloch parameters b and B. These parameters are plotted in Figs. 5 and 6, respectively. Figure 5 shows that the values of the exponent b are equal to the bulk value of $b = \frac{3}{2}$ for particle sizes greater than 6 nm diam for each system. For sizes less than 6 nm, the exponent decreases. This decrease is much more rapid for the [MgF$_2$]Fe system, which for the smallest size of 3 nm has $b = 0.37$.

Figure 6 shows that the Bloch constants for the two systems are roughly equivalent within an uncertainty of about a factor of two until iron core crystallite sizes less than or equal to 4 nm, where the [MgF$_2$]Fe system yields B values at least an order of magnitude larger than for [Mg]Fe. Both data sets approach the known bulk value for iron[20] as size increases.

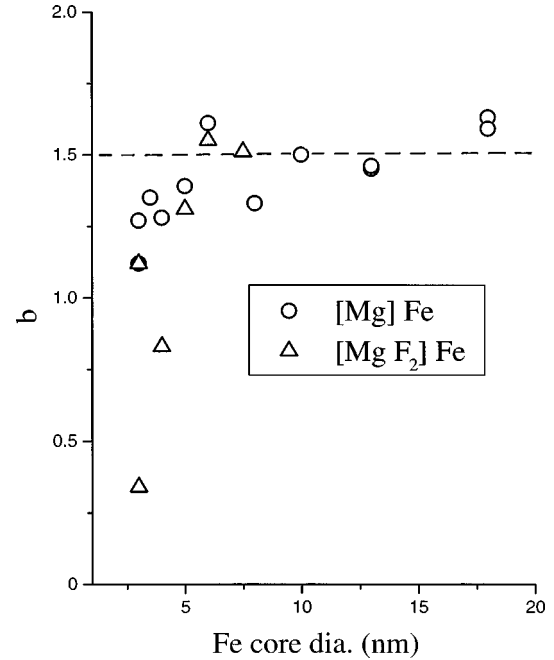FIG. 5. Bloch exponent as a function of iron crystallite size. Dashed line is the bulk value.

IV. 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 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 $M_s(T)$.

We reviewed previous work on the behavior of $M(T)$ for reduced dimension systems in the Introduction. The qualita-
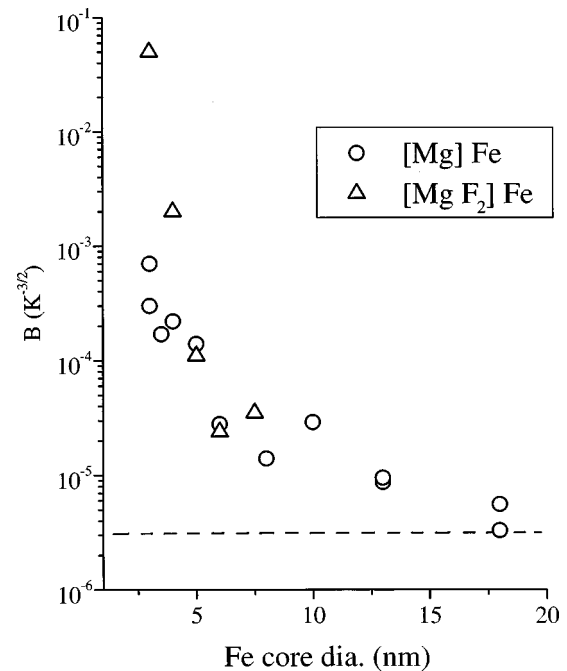

FIG. 6. Bloch constant as a function of iron crystallite size. Dashed line is the bulk value.

tive 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. We do not find the Bloch exponent larger than the bulk value as predicted and observed, for one single sized particle, by Hendriksen, Linderoth, and Lindgard and observed by us for a variety of sizes in MnFe$_2$O$_4$. Is the source of the experimental discrep-

ancy the fact that the samples of this present study are intimately interfaced with another material whereas the Fe-C of Linderoths *et al.* and our previous MnFe$_2$O$_4$ nanoparticles were not? Or does perhaps the difference lie in the magnetic material being metallic or nonmetallic? Xiao and Chien studied metallic, 2–3-nm iron in intimate contact with silica and saw $b = 3/2$, but with B an order of magnitude larger than the bulk. This is at least partially consistent with our present result and suggests that our future work should include [SiO$_2$]Fe.

In conclusion it appears that $M(T)$ behavior is richly dependent on size, interface, and the magnetic behavior. 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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