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Superparamagnetic behavior is investigated for Fe grown at 700 K onto MgO(001) to a thickness equivalent to that of a ten monolayer film. Two such Fe deposits separated by a 200-Å deposit of MgO exhibit a ferromagnetic response with no hysteresis at either 300 or 150 K, but with identical reduced magnetization curves $M(H/T)$ which confirms the existence of superparamagnetism. $M(H)$ data at 300 K were fitted to a Langevin function to yield an average particle size of 100 Å diameter. $M(T)$ for field-cooled and zero-field-cooled samples shows behavior characteristic of superparamagnetic particles with a distribution in particle size. Time-dependent remanent magnetization data measured over a 20 h period at various temperatures show nonexponential decay attributed to the distribution in particle size and interactions among the particles.

I. INTRODUCTION

In recent years, the phenomenon of superparamagnetism in a system of small ferromagnetic particles has attracted much attention[1] due to its relevance both in technological applications as well as in understanding the fundamental physics. Technologically, as the density of magnetic information-storage devices increases, the size of the ferromagnetic region approaches the superparamagnetic limit. Therefore, it is important to understand the thermal characteristics of the magnetization switching behavior in order to achieve higher, but stable, recording densities. From the fundamental point of view, the relaxation and switching behavior of a system of small, single-domain ferromagnetic particles is not well understood, partly because of the complicated nature of the interactions among the particles.[2–5] Also, a particle size distribution that is inevitably introduced in the materials-preparation process further complicates the situation[6] because the switching time or relaxation time depends on particle size. It was recently reported that, even for an isolated, single-domain ferromagnetic particle (i.e., no size distribution or interactions) the relaxation behavior does not follow expectation.[7] Quantum tunneling phenomena are also possible in small magnetic particles,[8,9] and this can further embelish the physics at low temperatures and introduce temperature-independent processes to consider.

Superparamagnetism[10] and the lack of hysteresis in the magnetization curve are well known. The theoretical treatment developed for ordinary paramagnetism can be extended whereby the Langevin function

$$L(x)=\coth x-\frac{1}{x}, \tag{1}$$

where $x=\mu H/k_BT$, is used, but with a value for the moment μ that is perhaps of order 10^5 times the atomic moment.

In the presence of an external magnetic field that is strong enough to overcome the anisotropy energy barrier ΔE, the magnetization direction of a single-domain particle aligns with the field. At time t after the field is abruptly removed, there is a finite probability that the magnetization has overcome the energy barrier and flipped due to thermal fluctuations. Under these conditions a collection of similar such particles undergoes a magnetization decay. Néel[11] argued that the decay is usually exponential to first order, so that one should observe the single relaxation rate approximation:

$$M_r(t)=M_0e^{-t/\tau}, \tag{2}$$

where M_0 is the initial magnetization. He also estimated the relaxation time τ of an isolated particle that leads to the relation

$$\frac{1}{\tau}=f_0e^{-\alpha}, \quad \alpha=\frac{\Delta E}{k_BT}. \tag{3}$$

For uniaxial anisotropy, ΔE is given by KV, where K is the anisotropy constant and V the particle volume. The prefactor f_0 is a constant, which Néel estimated to be of order 10^9 $\sec^{-1}$. Even though the assumptions that lead to Eq. (2) are sound, such simple decay behavior is not routinely observed in real systems.

In this paper we report on the superparamagnetic behavior of Fe(001) clusters grown epitaxially onto MgO(001) substrates. (The lattice mismatch is 3.8%.) The sample exhibits thermal-equilibrium superparamagnetic behavior at temperatures above 150 K for measurement times of order 10^2 sec. We extract the average island size and determine the average distance between islands. Temperature-dependent magnetization measurements for different initial conditions show typical behavior attributed to a particle size distribution. Time-dependent magnetization relaxation data do not follow a simple exponential form; instead logarithmic or power-law behavior suggests that interactions between particles play an important role.

In the following section we briefly describe our experimental procedures. In Sec. III, we present the results and a discussion. Section IV summarizes our findings.

II. EXPERIMENT

Fe was deposited on MgO(001) single-crystal substrates using electron beam evaporation in an ultrahigh vacuum

(UHV) chamber with a base pressure in the low 10^{-10} Torr range. The Fe was deposited to a thickness equivalent to that of a 14.3-Å film, which corresponds to 10 monolayer equivalents (MLE). The sample consists of two Fe deposits separated by a 200-Å MgO spacer. An additional 200-Å MgO capping layer was deposited on top to protect the sample when it is removed from UHV for the magnetic measurements. The thickness and deposition rate were monitored by a quartz-crystal microbalance. A stable rate as low as 0.05 Å/sec was achieved for both Fe and MgO evaporation by means of a feedback control system. The MgO layers were deposited directly from MgO single-crystal pieces. It was shown previously that MgO does not dissociate into ions[12,13] during the e-beam heating and evaporation process, as confirmed by x-ray photoelectron spectroscopy and diffraction (XPD).

Although both Fe on MgO(001) and MgO on Fe(001) grow epitaxially, as evidenced by XPD and reflection high-energy electron-diffraction studies, Fe does not grow in a layer-by-layer mode on MgO(001) substrates in the first few monolayers[14] at and above room temperature. However, 10-MLE-thick Fe deposits, grown at either room temperature or 400 K, do form continuous layers, are metallic, and exhibit full ferromagnetic remanence.[14] As discussed in the present paper, 10-MLE-thick films grown at 700 K show superparamagnetic behavior at room temperature. This suggests the formation of islands due to the increased mobility of the deposited species at elevated temperature. By 50-Å deposition of Fe, all films exhibit full ferromagnetic remanence (i.e., equal to the saturation magnetization value). We have grown the Fe at 700 K and used two Fe regions, separated by MgO, to increase the magnetic signal while each Fe region remains superparamagnetic. The resulting sample has the structure $[\text{MgO(200 Å)/Fe(10 MLE)}]_2$ on the MgO(001) substrate.

The sample was removed from UHV for the magnetic measurements which were carried out with a commercial superconducting quantum interference device (SQUID) magnetometer. The external magnetic field was applied in plane in the [100] direction of the MgO substrate, which is parallel to the Fe [110] direction. The MgO substrate exhibits a diamagnetic response in field. To correct for this we measured a bare MgO substrate separately and subtracted its signal from that for the magnetic sample. The diamagnetic MgO signal is nearly linear up to the maximum field of 10 kOe.

III. RESULTS AND DISCUSSION

Shown in Fig. 1 are the magnetization curves M(H) at several temperatures. The curves show no apparent hysteresis at 300, 150, or 100 K, while hysteric behavior is evident at 40 and 5 K. The hysteresis at low temperatures is due to long relaxation times compared with the measurement time, which is of order 10^2 sec. Since a close examination of the 100-K curve shows a small hysteresis, the blocking temperature must be between 150 and 100 K. Figure 2 is an $M(H/T)$ plot for magnetization curves at 300 and 150 K that show no hysteresis. This is a signature of superparamagnetism[10] that follows from the form of the Langevin function in Eq. (1). We use these nonhysteretic magnetization curves to estimate the average value of the effective magnetic moment μ per

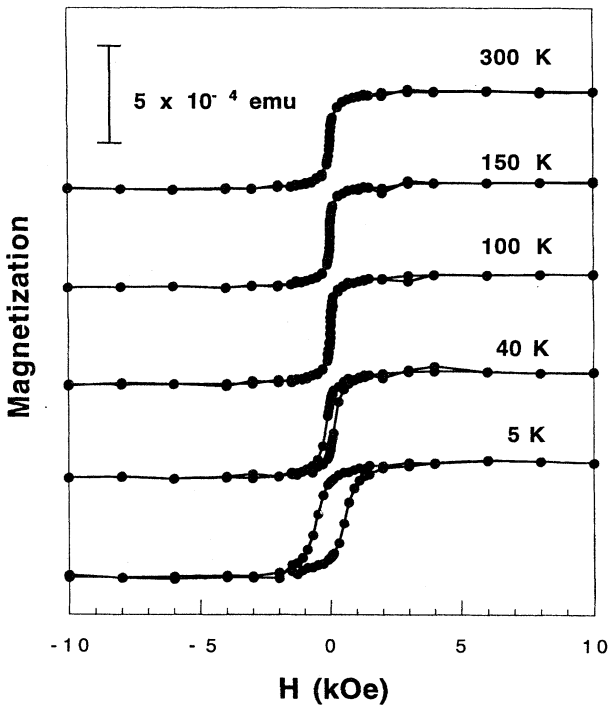

FIG. 1. Magnetization as a function of applied field H for two 14.3-Å equivalent thickness Fe deposits grown on MgO(001) at 700 K and separated and capped by 200-Å MgO deposits. Hysteretic behavior develops at the lower temperatures.

particle, in the absence of interactions, by fitting the data to the Langevin function to yield $\mu=(6.32\pm0.19)\times10^{-16}$ emu. Assuming a hemispherical shape of the particle, this value of μ corresponds to a particle size of $\sim$110 Å in diameter for the case in which bulk values of the atomic volume and magnetic moment are used. Since the amount of Fe deposited is equivalent to a 14.3-Å-thick film, it is possible to calculate an average distance of 50 Å between particle edges, or an average island density of almost 40%. This distance suggests that interactions between particles are not

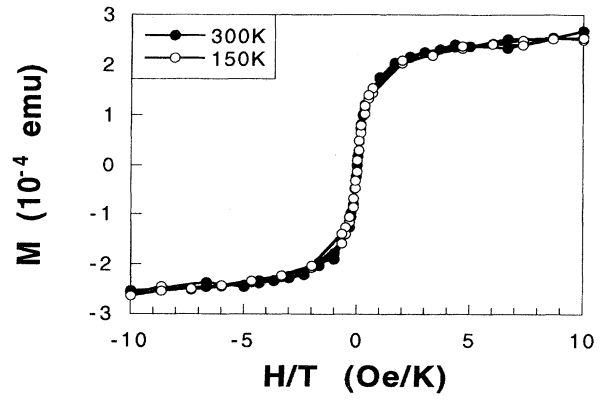

FIG. 2. Magnetization curve $M(H/T)$ at 300 and 150 K.

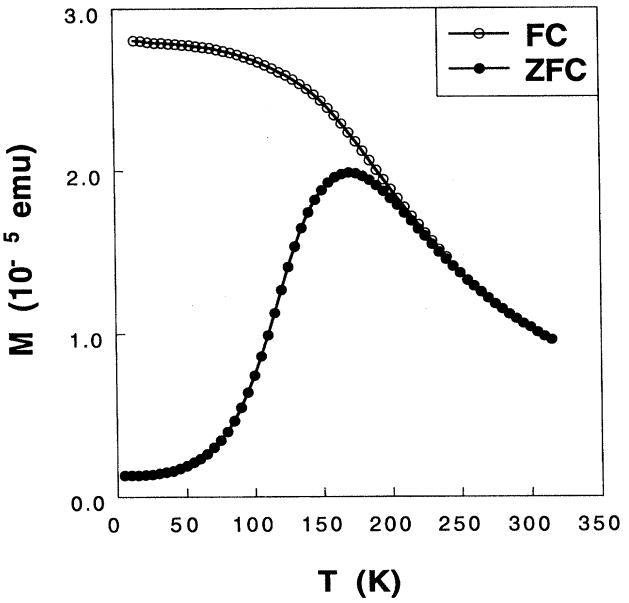

FIG. 3. Change of M with T. The curve denoted FC (field cooled) was measured for a sample cooled in 5 Oe and measured in that field on warming. The ZFC (zero-field-cooled) curve was cooled in zero field and subsequently measured in 5 Oe.

negligible. In the presence of interactions the local fields may be different than the applied fields, which could alter the above estimate of the effective moment. Even though it is difficult to determine particle size accurately in this way,[10] it is still a useful exercise to obtain an idea about the approximate size.

Figure 3 is the variation of magnetization with temperature for two different initial conditions. The curve denoted FC (field cooled) is for a sample initially cooled to 5 K in the presence of a 5-Oe applied field, and for which the magnetization was measured in the same field as the temperature is increased. The ZFC (zero-field-cooled) curve is for the sample initially cooled in zero field and then measured in 5 Oe. The origin of the characteristic peak in the ZFC curve and the monotonic decrease in the FC curve is typically attributed to the presence of a distribution of particle sizes that gives rise to a corresponding distribution in relaxation times, according to Eq. (3). For the FC curve, initially the magnetic moments of the particles are frozen along the field direction as they are cooled in the presence of an external field. This gives a large total magnetization at the lowest temperature. With increasing temperature, some particles have short enough τ so that the moment flips many times during the measurement time so that nothing is contributed to the net magnetization. The portion of such particles becomes larger with increasing temperature. Therefore, a decreasing total magnetization is observed. The peak in the ZFC curve can be understood in a similar way. The small applied field at the lowest temperature does not change the direction of the initially frozen moments in random directions. In other words, the relaxation time τ for most of the particles is much larger than the measurement time at the lowest temperature. As the temperature is initially increased, a portion of the particles whose τ is neither too large nor too small compared with the measurement time will align with the field during the measurement. This gives an initial increase in the net magnetization. With further increase of the temperature, the portion of the particles that align with the field changes according to the dependence of τ on temperature. Then a peak in the net magnetization occurs at the temperature where the largest portion of the particles can align with the field. At even higher temperatures, most of the particles have short enough τ in both the FC and ZFC cases that the two become indistinguishable. All of these features are observed in Fig. 3. If the measurement time determines the temperature at which the peak occurs in the ZFC curve, the peak position should changes for different measurement times. Even if there is no particle size distribution, a peak should still occur in the ZFC curve, but it should be narrow because all particles will align with the field at the temperature that matches with the measurement time.

Up to this point, we have not considered interactions between particles. Magnetization behavior similar to that of Fig. 3 was reported for a frozen ferrofluid[5] and attributed to dipolar interactions between the particles. The argument was based on the observation that the peak position did not change significantly for different measurement times. Inspired by this experiment, Mertens *et al.*[3] simulated the effect of interactions using local-mean-field theory and found that some of the experimental features could be reproduced if (i) the moments are inhomogeneously distributed in space and (ii) the system has a particular type of anisotropy. Explicit inclusion of interaction effects in the calculated τ yields a modified form of Eq. (3) that still retains its dependence on particle volume,[4,15,16] although the field dependence will be modified, as will any estimates of the particle-size distribution. Therefore, the observation of characteristic FC and ZFC curves similar to those in Fig. 3 by themselves do not necessarily exclude the existence of either interaction effects or particle-size distributions.

Although the theoretical determination of τ is not a trivial matter, as outlined by Aharoni,[6] it is possible to measure τ directly from experiment. The original thought experiment of Néel[11] suggested an ensemble of small particles put in a large field and then taken out to observe the remanent magnetization decay in time. If the decay follows the simple exponential form of Eq. (2), it is easy to determine τ by fitting the experimental data. Shown in Fig. 4 is the result of one such measurement at 40 K. We first applied a field of 10 kOe, and then reduce the field to 1 Oe and measure the remanent magnetization as a function of time. The magnetization decreases only $\sim 20\%$ over a 20-h time period. This is a slow relaxation behavior and indicates the stable nature of the system against thermal fluctuations at this temperature. But the decay is not a simple exponential. Figure 4 shows the relaxation behavior plotted on a log-log scale. Apart from the initial decay before 10 min, the plot yields a straight line. This implies that either a logarithmic form

$$M_r(t) = C - S \ln t, \tag{4}$$

where the constant S is the magnetic viscosity, or a power law,

$$M_r(t) = M_0 t^{-\beta}, \tag{5}$$

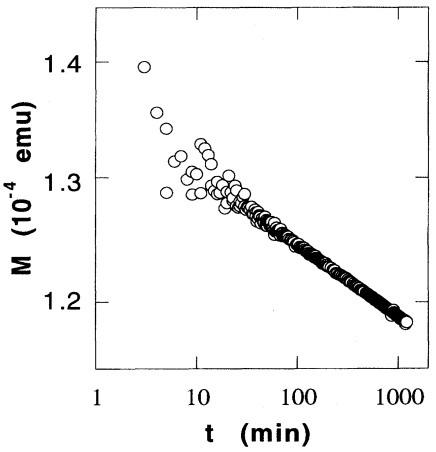

FIG. 4. Remanent magnetization measured on a log-log scale as a function of time at 40 K. The decay is not in the exponential form of Eq. (2).

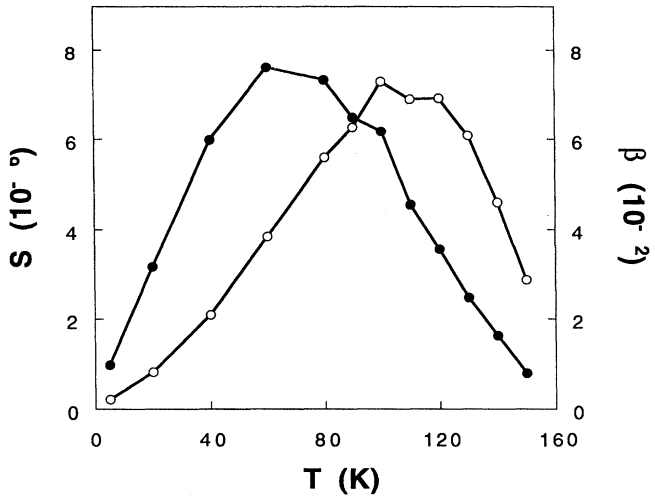

FIG. 5. Temperature dependence of the parameters S and β of Eqs. (4) and (5), respectively, extracted from fitting the data shown in Fig. 4. Regardless of the functional form of the decay, a peak is observed.

is appropriate to describe the decay process. Aharoni criticized[6] the use of Eq. (4) for lack of a physical basis, although it is used routinely.[5,9,17] Instead, he suggested to generalize Eq. (2) to

$$M_r(t)=M_0\int_0^\infty P(\tau)e^{-t/\tau}d\tau, \tag{6}$$

where $P(\tau)$ is the distribution function for τ. Because it is impossible to obtain an analytical form of this integral with the usual Gaussian form for $P(\tau)$, he instead used the Gamma distribution function and obtained a closed form for $M_r(t)$ which contains a modified Bessel function.[18] Our attempt at using a Gaussian distribution function and numerical integration to fit Eq. (6) to the experimental data did not give satisfactory results, which implies that this analysis, which is restricted to a system of noninteracting particles, may not be adequate for our system. Unless the particles are extremely far from each other, there exists a long-range dipolar interaction between particles.

The calculation of superparamagnetic relaxation times in real systems of interacting particles is a complicated problem even in the limit of weak interactions.[4] Logarithmic-type decay has been attributed to dipole-dipole interactions in frozen ferrofluid systems[5] rather than to the particle size distribution. Lottis *et al.*[2] incorporated dipolar interactions into the system in the form of a demagnetizing field and were able to find a decay curve that either resembles a stretched exponential or is logarithmic, depending on the time scale. These models, however, neglect that a distribution of particle size may play an important role in determining the functional form of the decay even without interactions. Alternately, it was recently reported[7] that even a single, isolated particle (that can have no possibility of interaction or size-distribution effects) does not show the simple exponential decay suggested by Eq. (2). Therefore, lacking a reliable theoretical model, we tried to fit the data with both the logarithmic and power-law functions mentioned above. Figure 5 shows the temperature dependence of the parameters S and β in Eqs. (4) and (5), respectively. These parameters represent a measure of the decay rate reminiscent of τ in Eq. (2). Nonmonotonic decay, such as in Fig. 5, has been observed in a number of other systems.[5,17,19,20] Due to the exponential nature of the dependence of τ on the particle volume and temperature in Eq. (3), there is only a narrow range in particle size for which relaxation phenomena can be observed within the time window of experimental measurement. Bean and Livingston[10] estimated that for a spherical Fe particle with only first-order crystal anisotropy, a particle 115 Å in radius will have a relaxation time of 0.1 sec at room temperature and will reach thermal equilibrium almost instantaneously. But a particle 150 Å in radius will have a relaxation time of 10^9 sec and will be extremely stable. The same arguments hold for the temperature dependence. One would expect a peak in the temperature dependence of the decay slope if the time window to measure the slope is fixed. In other words, if τ is too large compared with the measurement time (where the start time is a few minutes after the field is turned off) there will not be much decay within the experimental time window; or if τ is too short, most of the decay will have occurred before the measurement was performed.[2] In fact, this is the same reason why a peak in the ZFC curve should occur even with no particle size distribution. Just as we observed a broad peak in the ZFC curve of Fig. 3 due to the particle size distribution, peaks in Fig. 5 are also broad for the same reason.

From the observed decay rate at temperature T and the particle volume extracted from the Langevin function fit, one can estimate the fourfold, in-plane anisotropy constant K_1 in Eq. (3) where $\Delta E=K_1V/4$. For the 100-K decay, this leads to a value for K_1 between (5.2 and 6.7) $\times 10^6$ erg/cm^3 using the value of f_0 between 10^9 and 10^{13} sec^{-1}. This is an order of magnitude larger than the bulk Fe cubic anisotropy value of 5.4×10^5 erg/cm^3. There are two possible origins for this discrepancy. First, it is known[21] that the anisotropy constant increases as the particle size decreases because of the increasing importance of the surface anisotropy. This effect can

lead to an order-of-magnitude increase in the value of K_1 for the particle sizes under consideration. Second, the effect of interactions between particles can drastically change the relaxation time even when K_1 does not change much.[4,15,16] A recent experiment[7] using an isolated particle that showed nonexponential decay suggests that even for a single-domain particle the process of magnetization reversal can have an important effect on the decay behavior. For a system of particles the logarithmic or power-law decay is a result of a combination of particle size distribution and interaction effects. Although there are theoretical models that contain the elements of one or the other effect, it is important to develop a model that incorporates both to satisfactorily explain the experimental results.

IV. SUMMARY

The superparamagnetic behavior is investigated of Fe deposits grown at 700 K to 14.3-Å (ten monolayer) equivalent thickness. Two Fe regions separated by a 200-Å MgO spacer show no hysteresis at 300 or 150 K. Identical reduced magnetization curves $M(H/T)$ at different temperatures confirm that the system is superparamagnetic. Magnetization data taken at 300 K were fitted to a Langevin function to yield an estimated average particle size of 110 Å diameter. The change in magnetization with temperature for field-cooled and zero-field-cooled samples shows behavior characteristic of superparamagnetic particles with a particle size distribution. The time-dependent remanent magnetization was measured over a 20-h period at various temperatures. It shows nonexponential type decay, as had been reported in the literature for other systems. The distribution in particle size and the interactions among particles are believed to be responsible for the nonexponential decay observed.

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