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Monte Carlo simulations on the coercive behaviour of oxide coated ferromagnetic particles

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Abstract. The Monte Carlo simulation technique has been used to study the coercivity of small ferromagnetic particles covered by an antiferromagnetic shell. In particular, we examine its size and temperature dependence. We find that the exchange interaction between the ferromagnetic core and the antiferromagnetic shell of the particles causes a reversal in the size dependence of the coercivity at low temperatures. The enhanced interface anisotropy results in a considerable increase of the coercivity, and in a more rapid fall with temperature. Our simulations suggest that the steep temperature dependence of the coercivity observed in experiments, should be attributed to the strong temperature dependence of the anisotropy of the antiferromagnetic shell.

1. Introduction

The magnetic behaviour of small ferromagnetic particles has been studied for several years and was found to be very much size and temperature dependent. Recently many experiments have been concentrated on the effect of oxidation on the magnetic properties of ferromagnetic particles [1–7]. The small particles are readily oxidized when they are exposed in the atmosphere. The complete oxidation can be avoided by placing the particles in controlled oxygen atmosphere. In this way, an oxide shell is developed around the ferromagnetic core. In samples where the ferromagnetic core diameters were smaller than 10 nm [1] enhanced coercivities have been measured after the oxidation, whereas in samples with core diameters of the order of 50 nm, the coercive fields measured before and after the oxidation were not very different [5]. In Fe particles coated by an antiferromagnetic iron oxide with thickness 10–20 Å, the coercivity showed a large increase in samples with iron core diameter below 60 Å reaching a value about 2.7 kOe in a particle with core diameter 20 Å, whereas in samples with a larger core diameter the coercivity was almost constant, ∼250 Oe [1, 6]. The surface and interface effects between the oxide shell and magnetically hard Fe core were considered responsible for the high coercivity values observed at low temperatures and its drastic temperature dependence. The highest coercivity obtained in [1] at room temperature was 1050 Oe for a particle with a 140 Å core diameter, and its value at 10 K was 1425 Oe, whereas in a sample with core diameter 25 Å the coercivity decreased from a value of 3400 Oe at 10 K to a negligible value at 150 K. Thus, in the smaller particles the temperature dependence of the coercivity is much stronger than in the bigger particles. In smaller particles the Fe core feels much more the effect of the Fe-oxide shell, due to higher Fe-oxide to Fe ratio. The strong decrease of coercivity with temperature can be explained by the superparamagnetic behaviour of the Fe-oxide shell and its low blocking temperature. It is estimated that the Fe-oxide shell becomes superparamagnetic at $T \sim 10$–50 K [1, 6]. In all

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experiments on oxide coated particles, shifted hysteresis loops have been obtained at low temperatures. The loops become symmetric at temperatures above the blocking temperature of the oxide. The shifted hysteresis loop has been attributed to the exchange interaction between the ferromagnetic core and the oxide shell, which is unidirectional [1–5, 8].

The coercivity of single domain simple magnetic particles is well described by the phenomenological theory of Kneller and Luborsky [9]. A modification of this theory was developed by Trohidou *et al* [10] to incorporate the core-shell morphology and to explain the coercive properties of ultrafine iron particles coated by iron oxide. In this theory, the effect of a shell surrounding the core and of the interface and the surface, all with different anisotropy constants, is dealt with by substituting the magnetization and the anisotropy energy in the simple mean field theory by effective values that are determined by the structure of the particle. The model explained qualitatively the experimental data by considering one atomic layer thick interface with an effective anisotropy about ten times as large as that of the bulk Fe and a shell thickness of about 1.3 nm. In the mean field model the magnetic behaviour is attributed to the strong anisotropy at the interface between the core and the shell of the particle. A strong surface anisotropy is also considered as a candidate to explain the high observed coercivities. This model can only indicate the importance of the complex morphology of the particles without giving any insight in the physics originating from the ferromagnetic core-oxide shell morphology, that is thought to be responsible for the magnetic properties of the particles of interest. There are open questions about the effects owing to the microstructure of the particle, the ferromagnetic interaction between the spins in the core, the antiferromagnetic interaction in the shell and particularly the exchange interaction at the interface of the particle, as well as about the effect of temperature.

In a Monte Carlo simulation, the microstructure and the temperature are explicitly included and this method is therefore appropriate to study the magnetic behaviour of oxidized magnetic particles. The Monte Carlo results cannot be drawn by simple mean field arguments, although qualitative agreement with experiment can be obtained in both cases. Our simulations show that the exchange anisotropy owing to the interaction between the ferromagnetic core and the antiferromagnetic coating play a predominant role in the magnetic behaviour of the oxidized particles. The exchange anisotropy is not assumed beforehand in the simulation, but results from the microstructure that is absent in the mean field model. The effect of the exchange anisotropy is not incorporated in the effective uniaxial interface anisotropy of the mean field model, since it is a unidirectional anisotropy. In order to distinguish between the effects of interface and exchange anisotropy, we simulate the cases of a ferromagnetic shell and an antiferromagnetic shell. We find that the strong interface anisotropy causes an increase in the coercivity, but it does not explain itself the experimentally observed size dependence for all temperatures. Our simulations show that the temperature dependence of the anisotropy and in particular the steep decrease of the oxide shell anisotropy with temperature, fully account for the observed behaviour. In previous works, we showed that the orientation of the easy axis of the surface anisotropy has a significant effect on the coercivity [11, 12]. The radial surface anisotropy considered in our Monte Carlo simulation is more realistic and its effect on the magnetic behaviour is very different from that of the constant easy axis surface anisotropy considered in the mean field model. The actual behaviour of the oxidized particles is attributed to different physical reasons in the two works and it is therefore apparent that the Monte Carlo simulation gives more physics insight in the particles of interest.

In this work we simulate spherical magnetic particles with core-shell morphology. We use as parameters the particle size R, the exchange coupling J, the four anisotropy coupling

constants K for different parts of the particle and the lattice structure. We present results for a set of these parameters in order to discuss the physics emerging from some morphology characteristics of our system. So, for a particular magnitude of J we are interested in the ferromagnetic ordering in the core and the antiferromagnetic ordering in the shell, we consider values of R that allow us to examine the size dependence observed in experiments, and finally for a particular value of anisotropy constant of the core, we use relative values for the anisotropy constants in different parts of the particle following the experimental evidence as explained in section 2 where the simulation method is described. We consider two values of the anisotropy constant of the interface in order to examine the effect of neglecting the interface anisotropy and of including an interface anisotropy one order of magnitude higher that in the core. In our work, we start with a given set of parameters for simple ferromagnetic particles with well understood behaviour and we examine the effect of adding one by one, factors that are present in the real systems. In this context, we choose simple cubic lattice structure for the core and the shell since the obtained qualitative conclusions are not expected to change by the lattice structure.

2. Simulation method

We use the standard Metropolis algorithm to simulate our system. We consider a simple cubic lattice and we define a spherical particle of radius R by fixing the origin at a certain site and including all the sites within a distance of R lattice spacings. The shell is considered as a layer surrounding the core and being four lattice spacings wide. The interface between the core and the shell is defined by the spins in the outer layer of the core being one lattice spacing thick. The surface of the particle is defined by the spins in the two outer layers of the particle, with two lattice spacings thickness. The spins interact with classical Heisenberg exchange interactions. For fine particles, there is some evidence that the easy axis is uniaxial, even though in bulk materials the easy axis is not uniaxial but along the three cubic axes [13]. The core is always considered ferromagnetic with a uniaxial anisotropy. The anisotropy coupling constant of the core is denoted by K_C. Since the bulk anisotropy of the oxides is lower than that of the corresponding ferromagnetic materials, for illustration, we consider that the anisotropy coupling constant of the antiferromagnetic shell is again uniaxial with the same easy axis as in the core and with a coupling constant, K_{SH}, of magnitude one quarter of K_C. Many studies [14] have shown that due to the reduced symmetry of the surface, the surface crystal anisotropy is stronger than the bulk, the same argument holds obviously for the interface. In our simulation, we always consider that the spins in the interface have the same type of anisotropy as in the core with an anisotropy coupling constant, K_{IF}, one order of magnitude higher than K_C. The easy axis of the anisotropy at the surface of the particles is assumed to be radial, i.e. perpendicular to the surface at each surface site [15]. The anisotropy coupling constant at the surface, K_{SRF}, is one order of magnitude higher than that in the shell.

The energy of the system in the presence of an external magnetic field is

$$E = -\sum_i \sum_{j \neq i} J_{ij} \boldsymbol{S}_i \boldsymbol{S}_j - \boldsymbol{H} \cdot \sum_i \boldsymbol{S}_i - \sum_i K_i S_i^2 \cos^2 \varphi_i \tag{1}$$

where S_i is the atomic spin at site i. The first term gives the Heisenberg exchange interaction between the spins. Here, J_{ij} is the exchange coupling constant between the nearest neighbours at sites i and j. J_{ij} is equal to $J(>0)$ for spin sites i and j in the ferromagnetic core, whereas it is equal to $-J$ when at least one spin site is in the antiferromagnetic shell. The second term expresses the energy in the presence of an external magnetic field. In the

simulation, the magnetic field is expressed in units of $2J/g\mu_B$. The third term corresponds to the anisotropy energy. K_i stands for the uniaxial anisotropy coupling constant at site i and is expressed in units of $2J$. The anisotropy coupling constant parameters used in the simulation are: $K_C = 0.1$, $K_{IF} = K_C$ or $K_{IF} = 10K_C$ (enhanced interface anisotropy), $K_{SH} = 0.025$, $K_{SRF} = 10K_{SH}$ or $K_{SRF} = 10K_C$ in the case of simple ferromagnetic particles. Finally, φ_i is the angle between S_i and the direction of the easy axis at i. We also note that the temperature is expressed in units of J/k_B. In the units used in our model the critical temperature for all particles is considered to be 2.9 [16].

In order to determine the coercive field, we start with the spins in the $+z$ direction. A magnetic field is applied in the $-z$ direction. The coercive field is defined as the magnetic field that reverses the magnetization of the particle in the simulation time, so that the z-component of the magnetization vanishes. In our simulations we have used 2×10^4 Monte Carlo steps per spin. We have checked our results by calculating the coercivity for different sequences of random numbers. Here we present our results over five runs. The statistical error that we found was smaller than the error introduced by the division step used to determine the coercive field, i.e. 0.01 in our units and only at the highest temperatures it was comparable to it. Including the corresponding error bars in our figures would not affect the information obtained from them so they are left out.

3. Results and discussion

3.1. Particles coated with a ferromagnetic shell

We consider first the case of spherical single domain particles composed of a ferromagnetic core and a ferromagnetic shell with anisotropy lower than that in the core. We will call them composite particles from now on. The results of the simulation, with the parameters described in section 2, are presented in figures 1 and 2 for two composite particles with

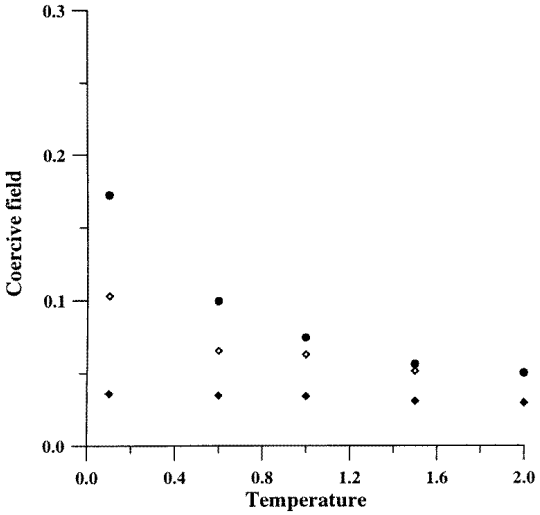

Figure 1. Coercive field against temperature for a spherical particle of radius $R = 8$. The full circles correspond to the simple ferromagnetic particle and the diamonds to the composite particle, for $K_{IF} = K_C$ (full diamonds) and $K_{IF} = 10K_C$ (open diamonds). The anisotropy constant parameters are given in section 2 of the main text.

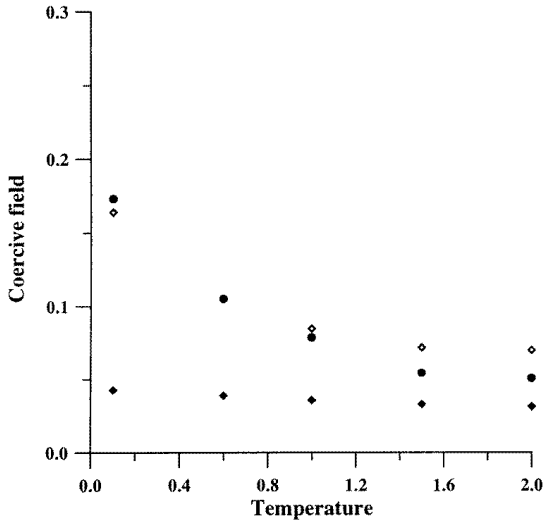

Figure 2. Coercive field against temperature for a spherical particle of radius $R = 10$. The circles correspond to the simple ferromagnetic particle and the diamonds to the composite particle, for $K_{IF} = K_C$ (full diamonds) and $K_{IF} = 10K_C$ (open diamonds).

radii $R = 8$ ($N = 2109$ spins) and 10 ($N = 4169$ spins) respectively. The particles have a surface two lattice spacings thick and radial surface anisotropy. In figures 1 and 2, we have also plotted the coercive fields of two spherical ferromagnetic particle of radii $R = 8$ and 10, with core anisotropy constant $K_C = 0.1$ and radial surface anisotropy constant $K_{SRF} = 1.0$ (circles in figures). The coercive behaviour of the simple ferromagnetic particles is well understood by means of mean field theory [9] and the effect of the surface anisotropy is discussed in [12]. Let us now turn to the composite particles. If we initially consider an interface anisotropy equal to the core anisotropy, we observe that the low anisotropy ferromagnetic shell results in a significant reduction of the coercivity for both particles (full diamonds in figures). The coercive fields of the smaller particle are slightly lower than those of the bigger one. In both cases, the coercivity is weakly dependent upon the temperature. We allow next for an interface anisotropy one order of magnitude higher than that in the core (open diamonds in figures). As it can be seen in figures 1 and 2, the coercivity has increased in both particles, but more significantly in the bigger particle. In the presence of an enhanced interface anisotropy, the coercive fields exhibit a considerable decrease with temperature. In figures 1 and 2, we can see that the coercivity of the simple ferromagnetic particles is much higher than that of the composite particles with $K_{IF} = K_C$, and it is slightly higher in the case of the enhanced interface anisotropy. If we could attribute an effective anisotropy to the composite particle, then obviously, this effective anisotropy would be much lower than that of the simple ferromagnetic particle. This fact can explain the lower coercive fields of the composite particle. Including the enhanced interface anisotropy we increase the effective anisotropy of the composite particle significantly, but it is still slightly lower than that of the simple one. The effect of the interface anisotropy is more pronounced in the bigger particle because of the larger number of sites on the interface.

We have examined the case of the ferromagnetic particle coated by a ferromagnetic shell of lower anisotropy than the core, in order to distinguish the anisotropy effects from the exchange interaction effects. Now, we proceed with the experimentally interesting case of an antiferromagnetic shell.

3.2. Particles coated with an antiferromagnetic shell

We consider now ferromagnetic particles coated with an antiferromagnetic shell, with anisotropy parameters as described in section 2. We will refer to these particles as oxidized particles. The difference between the composite and the oxidized particles is, therefore, the type of the exchange interaction in the interface and the shell of the particles. The magnetization per spin of the ferromagnetic particles is only slightly dependent on the particle size. We find that the antiferromagnetic shell results in a reduction of the magnetization per spin, that becomes stronger as the oxidized particles become smaller. This behaviour is related to the higher shell to core ratio in the smaller particles, resulting in a much higher contribution from the antiferromagnetic shell and is consistent with experimental findings on Fe particles coated by an Fe-oxide, where the magnetization was found to increase with particle size [5].

The results of our simulations for the coercivity of two oxidized particles with sizes $R = 8$ and $R = 10$ are shown in figures 3 and 4 respectively. In the same figure we have also plotted the coercivity of two simple ferromagnetic particles of the same size with the oxidized particles and anisotropy parameters as described in section 3.1. We first considered the case of an antiferromagnetic shell with interface anisotropy equal to the core anisotropy (full diamonds in figures 3 and 4). By comparing the coercive field values in this case with those of the simple particles, we see that there is a small difference in magnitude between them. The coercive fields of the oxidized particles are slightly higher and they exhibit a weaker temperature dependence. What is remarkable here, is that there is a reversal in the size dependence of the coercivity. The smaller particle has higher coercive fields than the bigger. This effect has been produced by the presence of the antiferromagnetic shell itself, and it is not an effect of the reduced anisotropy of the shell, since it is not observed in the case of the ferromagnetic coating. From the simulation it turns out that this effect should be attributed to the exchange interaction between the ferromagnetic core of the particle and the antiferromagnetic shell. This interaction has the same effect as an extra unidirectional

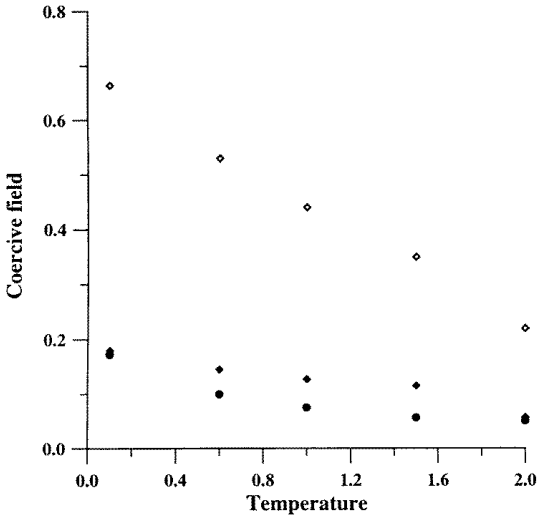

Figure 3. Coercive field against temperature for a spherical particle of radius $R = 8$. The circles correspond to the simple ferromagnetic particle and the diamonds to the oxidized particle, for $K_{IF} = K_C$ (full diamonds) and $K_{IF} = 10K_C$ (open diamonds).

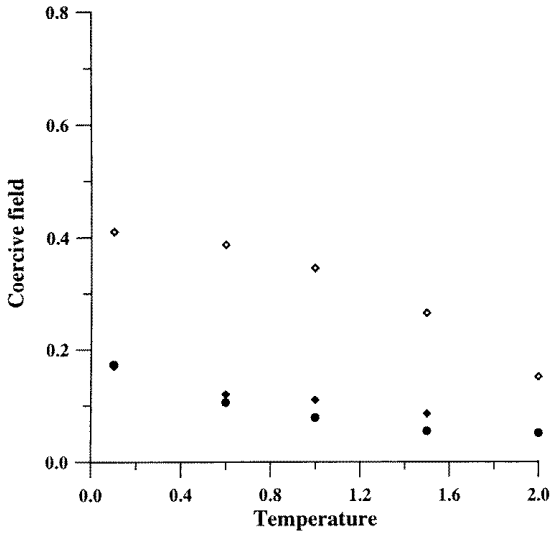

Figure 4. Coercive field against temperature for a spherical particle of radius $R = 10$. The full circles correspond to the simple ferromagnetic particle and the diamonds to the oxidized particle, for $K_{IF} = K_C$ (full diamonds) and $K_{IF} = 10K_C$ (open diamonds).

interface anisotropy as has been described in earlier works [2–4] and is known as exchange anisotropy [8]. In figures 3 and 4, we can also see the effect of the enhanced interface anisotropy (open diamonds). This anisotropy causes a considerable increase in the coercive fields of both particles. As can be seen in figures 3 and 4, the effect on the smaller particle is more drastic, so that its coercivity is much higher than the coercivity of the big particle for all temperatures. The enhanced interface anisotropy causes an enhancement to the effect induced by the exchange anisotropy in the interface. They essentially result in a pinning of the magnetic moments in the interface. The interface anisotropy introduces a steep temperature dependence in agreement with the experimental findings for the coercivity of the small Fe particles [1, 3].

Finally, we investigated the effect of the temperature dependence of the anisotropy coupling constant on the coercivity. The following expression for the temperature dependence of the anisotropy $\kappa_l(T) = \kappa_l(0)\hat{\mathbf{I}}_{l+1/2}(\hat{\mathbf{I}}^{-1}_{3/2}(m))$, where the $\hat{\mathbf{I}}$s are hyperbolic Bessel functions and m is the magnetization at temperature T, was proposed many years ago by Callen and Callen [18] . We assume that our values of the anisotropy follow this form for $l = 4$ which is appropriate for our lattice. It displays a close to exponential fall-off of K_{SH} with T and becomes negligible for $T > 1.0$, while for K_C the temperature dependence is smoother. The temperature dependence of the anisotropy and coercivity is in good agreement with the experimental findings [1, 6, 17, 18]. The results are shown in figure 5 for two particles with considerably different radii, $R = 10$ ($N = 4169$ spins) and 20 ($N = 33401$ spins) (squares and diamonds respectively). It is seen that the temperature dependence of the anisotropy results in a steep decrease of the coercivity with temperature for the smaller particle. The coercive fields of the big particle vary less rapidly with temperature. The size dependence of the coercivity exhibits a low temperature cross-over, at $T \sim 0.5$. Above this temperature, the coercive fields of the particle with $R = 10$ are lower than those of the particle with $R = 20$. Our results therefore indicate that the low

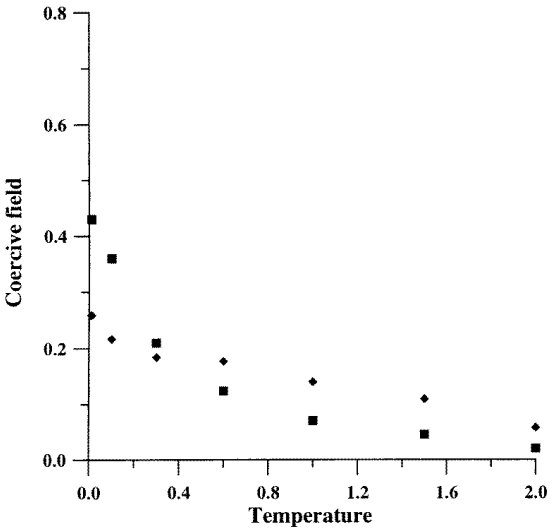

Figure 5. Coercive field against temperature for oxidized particles of radii $R = 10$ (squares) and $R = 20$ (diamonds). The anisotropy coupling constants of the core, interface, shell and surface are temperature dependent as described in the main text.

cross-over temperature observed in experiments [1] should be attributed to the temperature dependence of the anisotropy.

4. Conclusion

We have presented Monte Carlo simulation results on small ferromagnetic particles covered by an antiferromagnetic shell. We have started with a set of parameters for simple ferromagnetic particles and examined the effect of adding one by one the factors that are present in real systems. Our work proves the inadequacy of mean field models to indicate the physical reasons that explain the observed properties of small magnetic particles. The simulation results are in qualitative agreement with the experimental observations and give a physical insight to the properties of the oxidized magnetic particles. We conclude that the exchange interaction between the antiferromagnetic shell and the ferromagnetic core plays a predominant role in the magnetic properties of particles with big shell to core ratio and at low temperatures. This interaction causes a reversal in the size dependence of the coercivity at temperatures well below the blocking temperature of the antiferromagnetic coating. The temperature dependence of the anisotropy is also found to contribute to the strong temperature dependence of the coercivity of the small oxidized particles.

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