The influence of shape and structure on the Curie temperature of Fe and Co nanoparticles

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(Presented on 1 November 2005; published online 21 April 2006)

We have investigated the effect of lattice fluctuations on the magnetic properties of nanoparticles of Fe and Co. Atomic structures were simulated using a molecular-dynamic approach, with the system slowly cooled into the ordered phase. The magnetic properties were then simulated using an atomistic approach using a classical spin Hamiltonian taking into account the long-range nature and atomic separation dependence of the exchange. The magnetic properties are found to be affected by both the particle shape and the lattice fluctuations. For a perfectly ordered lattice we find that a spherical particle has a larger magnetization for a given temperature than a cube containing the same number of atoms. We have also studied the effect of lattice fluctuations. This involves a comparison of $M(T)$ for two cases, firstly, a nanoparticle with a fixed lattice corresponding to the low-temperature annealed state ($T=20$ K), and secondly a nanoparticle with a lattice structure equilibrated at the temperature T, the latter case being subject to fluctuations in the lattice spacing, and the nanoparticle shape. The dynamic structure gives rise to a reduction in the magnetization and T_c, which is a finite size effect to be considered beyond others such as the reduction in coordination at the nanoparticle surface. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2167636]

I. INTRODUCTION

As the bit density for magnetic data storage increases, increasingly small nanoparticles are required to store the information in a stable way. This presents a number of engineering challenges, but in addition to this the study of finite-size effects in these small particles becomes critical to our understanding of the underlying physics. For very small particles, of 5 nm or less in diameter, atomistic scale modeling is better suited than micromagnetics to study these effects. At the atomistic scale it has been found that the shape of particle used can significantly affect the magnetic properties of the system.[1] As a result, realistic particle shapes should always be used. Another aspect of finding the realistic particle structures involves variations in internal atomic structure. In particular, it might be expected that the lattice fluctuations would be rather different in nanoparticles from bulk materials. This leads naturally to local fluctuations in the exchange energy, with possible consequences for the magnetic properties. In this paper, we use a combination of molecular dynamics and atomistic spin models to investigate the effects of particle shape and lattice fluctuations on the magnetic properties of Fe and Co nanoparticles. Both effects are found to contribute to a change in the Curie temperature.

II. MODELING METHODS

In order to obtain realistic shapes and lattice structures of the nanoparticles, a molecular-dynamic approach was used to simulate the annealing. Simple pair potentials, such as Lennard-Jones potentials are not suitable to reproduce the specific properties of metals, such as elastic constants, thus the embedded atom method (EAM) was utilized.[2,3] Low-temperature annealed atomic microstructures were produced as follows. The initial perfect-crystal configuration was heated up to 1500 K. Annealing was simulated by subsequently cooling down the system in 20 K steps. At each temperature step, 60 000 molecular-dynamic integration steps were performed. Free boundary conditions were used to allow the system to develop its characteristic shape.

The dynamic magnetic calculations were performed by numerical solution of the Landau-Liftshitz-Gilbert (LLG) equation for the magnetic system. The model used an atom-

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istic approach with the Heisenberg form of exchange similar to Nowak *et al.*[4] The time evolution of the magnetization was calculated using the Langevin dynamics, essentially the Landau-Liftshitz-Gilbert equation augmented by a random field term to introduce thermal activation. The variation of the magnetization with temperature was simulated for particles with a perfect bcc structure, with spherical, cubic, and annealed particle shapes. For comparative purposes the bulk calculations were approximated using an 8-nm-diam particle (25 000 atoms). These calculations were performed by cutting a large spherical particle from a bulk structure, incorporating no finite-size effects such as variation in lattice spacing or structure as a function of temperature. These larger "bulk" particles were not annealed due to computational requirements and the fact that their magnetic properties are dominated by bulk parameters. The spin moments are initialized pointing in the easy axis direction, i.e., an ideal 0 K configuration. The temperature was then increased in 20 K steps in keeping with the molecular-dynamic calculations, and the system was equilibrated before taking time-averaged measurements of the mean magnetization of the particle. The system was then reset and the simulation was repeated 500 times to calculate the average magnetization and the standard error. During the annealing process the structure of the particle changes significantly and so additionally the variation of magnetization with temperature was calculated for the dynamic particle as well, at each temperature step incorporating any structural changes following from the molecular-dynamic calculations, and by default, any corresponding changes in exchange energy. The major challenge with modeling the magnetic properties of a particle with a nonperfect crystal lattice is calculating the Heisenberg exchange energy between the spins, since the atoms are no longer confined to particular lattice sites. This would require fairly detailed and extensive *ab initio* calculations for even the smallest of systems, and so in this study exchange interaction as a function of atomic separation has been approximated by assuming an a Ruderman-Kittel-Kesuya-Yoshida (RKKY)-type interaction. Exchange parameters previously published for perfect iron and cobalt lattices,[5] were used to model the variation of the Heisenberg exchange as a function of atomic separation. However, since the Heisenberg exchange is spatially inhomogeneous these points did not conform to an RKKY curve of a single frequency and so a polynomial approximation through the points was used to define the exchange at a given atomic separation. In order to achieve an accurate value for the Curie temperature the maximum number of interactions from the available data was used in all the calculations.

III. RESULTS

The simulated annealing process was found to give a significantly different shape and structure to that of a spherical particle consisting of the same number of atoms but with a perfect bulk lattice structure. Figure 1 shows the structure of an annealed 672-atom Co particle in comparison with a spherical particle. The immediately obvious difference in the annealed particle is the faceting not present in a perfectly spherical particle. These differences in shape are important

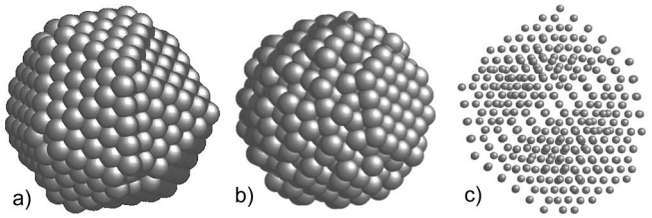

FIG. 1. (a) Simulated annealed Co particle showing faceting. (b) Spherical Co particle. (c) Transparent view of Co particle in (a).

for the Curie temperature calculations, since the shape determines the number of surface atoms whose reduced coordination number will affect the exchange energy locally. Also important are fluctuations in the atomic positions, since any change in interatomic spacing will have an impact on the Heisenberg exchange. We characterize these fluctuations by calculating the variation in mean atomic separation at each atomic site as a function of the distance of an atom from the center of the particle, results for a 672-atom cobalt particle being shown in Fig. 2. As it can be seen there is a roughly constant scatter in the mean atomic spacing of around 0.5 nm arising from the finite temperature of the annealed particle. We note that at the surface of the particle there is an inward relaxation in the lattice spacing. This could be related to the surface potential, since a similar effect has previously reported in *ab initio* calculations.[6] There is also a significant compression towards the center of the particle. The physical origin of this is thought to be the same as that for the compression at the surface, but arising from a visible dislocation in the particle. Using the magnetic model as described above, and using perfect lattice structures and those predicted by the molecular-dynamics (MD) model the Curie temperatures of different shapes and structures of particle were compared. Figure 3 shows the temperature dependence of the magnetization for a 672-atom Co particle, giving a comparison of the behavior of a cube, a sphere, and an annealed (faceted) particle with that of the behavior of a bulk material. As previously suggested[1] there is a decrease in the Curie temperature when comparing a cube with a sphere, as shown in Fig. 3. This is caused by the cube having a greater surface area

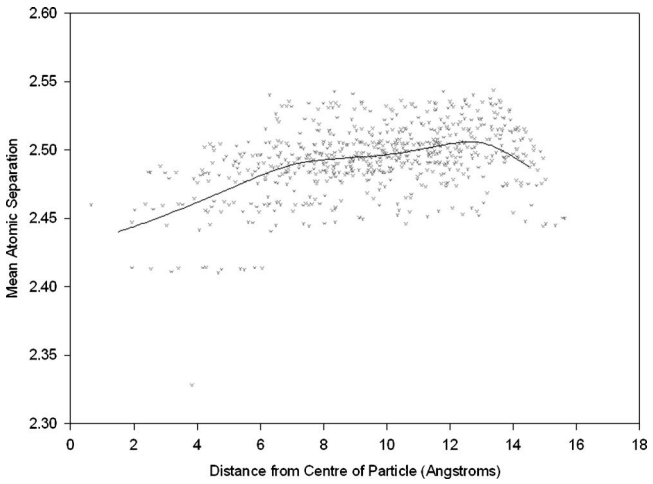

FIG. 2. Graph of mean atomic separation vs distance from center of particle for a 672-atom Co particle.

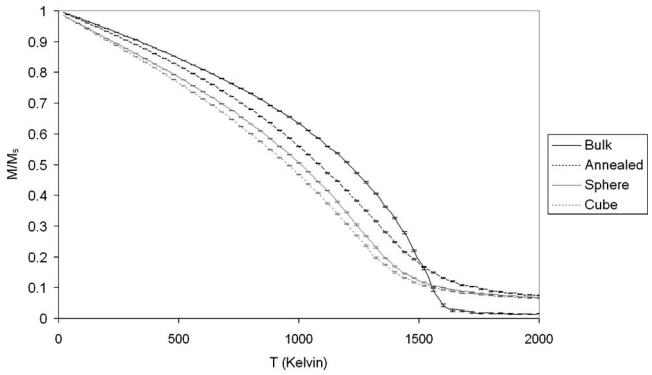

FIG. 3. Graph of M vs T for different particle shapes of a 672-atom Co particle.

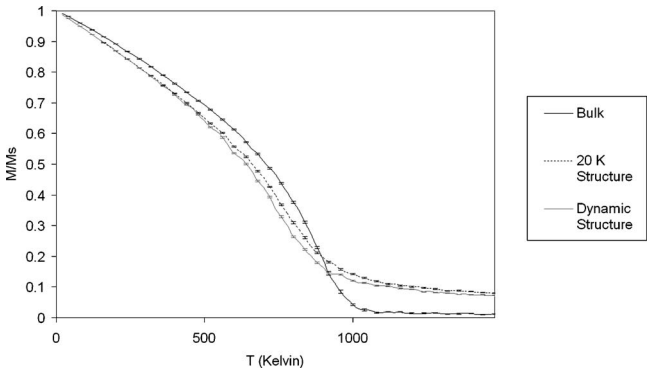

FIG. 4. Graph of M vs T for dynamic and static particle structures of a 432-atom Fe particle.

leading to a reduction in the exchange coupling due to the larger number of missing neighbors, giving rise to a reduced Curie temperature. By comparison the annealed particle showed a significant increase in the Curie temperature compared to the spherical particle above. This is largely due to the compressions in the center and surface of the particle, which in cobalt leads to an increase in the exchange for the first- and second-nearest neighbors. A similar comparison of a 432-atom iron particle was made, and showed the same trends, although the effect was less pronounced due to the long-ranged nature of the exchange in Fe in contrast to Co where the exchange is dominated by the short-ranged interactions. It is interesting to note that the residual magnetization above the Curie temperature, arising from the small size of the systems. The exchange interaction is strong enough to induce short-range correlations of the moments even at temperatures $>T_c$. In a large system, of size $\gg$ correlation length there are sufficient magnetic moments to ensure that the net magnetization goes to zero. As the size of the system is reduced to values close to the correlation length, however, it becomes more difficult for the system to achieve a zero net magnetization, at least until the correlations are completely destroyed at temperatures much greater than T_c. This effect leads to a broadening of the ferroparamagnetic transition, which becomes more pronounced as the particle size is reduced. The final effect investigated was that of changes in the crystal lattice with temperature on the magnetic properties using as an example a 432-atom iron particle. As the temperature increases there are increasingly large thermally induced fluctuations of the lattice, which might be expected to be relatively large in small particles. This was performed by substituting different atomic structures for a given temperature, obtained from the annealing simulation. The variation of M with T is compared with the "static" case (using the low-temperature annealed microstructure) and also calculations for a bulk material in Fig. 4. The expansion of the lattice leads to a lowering of the magnetization at a given temperature and a decrease in the Curie temperature. In iron the largest contribution to the exchange is from the nearest atomic neighbors. At that distance the slope of $J_{ij}(r)$ is negative, leading to a decrease in the exchange and thus the Curie temperature. This effect is material dependent, however, since it depends on the particular form of the exchange interaction.

IV. CONCLUSION

We have used a combination of molecular dynamics and atomistic magnetic modeling to study the effects of lattice and shape fluctuations on the static magnetic properties of the nanoscale Co and Fe particles. Simulated microstructures show the expected faceting which gives a large difference in the predicted magnetic properties when compared with ideal shapes such as cubic and spherical particles. The differences are sufficiently large to suggest that simulations of the magnetic properties of nanoparticles small enough to be dominated by surface properties should be carried out using realistic particle shapes in order to introduce the correct number of surface atoms with reduced coordination number. These effects are exacerbated by a reduction in the average spacing of the surface atoms, leading to variations in the exchange coupling of surface atoms. A further effect, normally neglected in nanoparticle simulations is the lattice fluctuations, which increase with increasing temperature. Due to the resulting exchange fluctuations, these have been shown to give rise to significant deviations in the magnetization relative to values calculated using a constant (temperature invariant) microstructure. These are finite-size effects beyond those normally considered in nanoparticle simulations. The results presented here suggest that the development of the atomistic simulations of the magnetic properties of nanoparticles should be accompanied by realistic MD calculations of their lattice structures.

ACKNOWLEDGMENT

One of the authors (R.E.) is grateful to Seagate Research for the provision of a research studentship.

[1]K. Binder *et al.*, *Monte Carlo Methods in Statistical Physics* (Springer-Verlag, Berlin, 1979), p. 204.
[2]M. S. Daw and M. I. Baskes, Phys. Rev. B **29**, 6443 (1984).
[3]X. W. Zhou *et al.*, Acta Mater. **49**, 4005 (2001).
[4]U. Nowak, O. N. Mryasov, K. Y. Kushen Ko, and R. W. Chantrell, Europhys. Lett. **69**, 805 (2005).
[5]M. Pajda, J. Kudrnovsky', I. Turek, V. Drchal, and P. Bruno, Phys. Rev. B **64**, 174402 (2001).
[6]A. V. Postnikov, P. Entel, and J. M. Soler, Eur. Phys. J. D **25**, 261 (2003).