

# Surface induced suppression of magnetization in nanoparticles

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## Abstract

A model based on competing exchange interactions is presented for the investigation of nanoparticle magnetization. The ferromagnetic (FM) and antiferromagnetic (AFM) exchange interactions contribute differently at the nanoparticle surface and interior, leading to reduced ferromagnetic order at the surface. This model predicts an unconventional temperature dependence of magnetization and a surface magnetically 'dead layer'. This is confirmed by temperature dependent magnetization and Mössbauer measurements of FePt nanoparticles. The effects are sensitive to particle size and surface terminations.

(Some figures in this article are in colour only in the electronic version)

Nanoparticle magnetism is a subject of active research because of its potential applications in data storage, spintronics and biomedicine [1]. The size and temperature dependence of magnetization as well as magnetization reversal were studied both experimentally and theoretically in a variety of systems [2–7]. The results are system dependent suggesting strong effects of the surface and the nature of magnetic interactions in nanoparticles. The surface effects were studied theoretically in various aspects. First, the surface may introduce large magnetocrystalline anisotropy because of its lowered symmetry. Second, the exchange interaction near the surface can be modified because some neighbouring atoms are missing and the electronic structure of surface atoms is different from its bulk counterparts.

While the enhancement of saturation magnetization ( $M_s$ ) is observed in small elemental metallic clusters [7], many thin film and nanoparticle systems (commonly oxides) have reduced  $M_s$  [8]. Earlier, this effect was explained by a magnetically 'dead layer' [9], or random canting of the surface spins caused, for example, by competing AFM exchange interactions between sublattices [10]. Other studies suggest that the spin canting persists throughout the volume of the particle, and therefore a finite size rather than surface effect [11]. To further complicate the issue, both theoretical and

experimental work suggest that surface atoms may have either enhanced or quenched moment, depending on their chemical environment [12, 13].

In this paper we show that the competition between FM and AFM interactions in nanoparticles can lead to surface induced suppression of the magnetization. The symmetry of surface termination of the nanoparticle may lead to a magnetic structure that is paramagnetic, non-collinear or FM, depending on the relative strength of the competing exchange interactions. We consider model particles with the shape of truncated octahedron (TO) terminated by (1 1 1) and (0 0 1) facets, mimicking experimentally synthesized nanoparticles [14]. The surface ordering temperature can be lower than that of the interior of the particle, resulting in a magnetically 'dead layer' at finite temperatures. This model is consistent with several of our experimental observations in FePt nanoparticles: (1) a significant paramagnetic volume fraction at finite temperatures, which is enhanced with decreasing particle size and diminished by cooling; (2) a large reduction of the zero temperature magnetization from bulk values; (3) an unconventional temperature dependence of the magnetization which becomes more prominent in smaller sized particles.

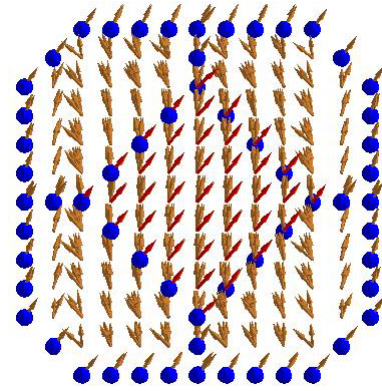
For simplicity, we consider a model nanoparticle with the simple cubic (SC) lattice. The competing exchange interactions are modeled with nearest neighbours (NN) being FM and second nearest neighbours (SNN) AFM. We use the Heisenberg model Hamiltonian in the external field,  $B_{\text{ext}}$

$$H = J_{01} \sum_{\alpha \text{ NN}} \vec{S}_i \cdot \vec{S}_j + J_{02} \sum_{\beta \text{ SNN}} \vec{S}_i \cdot \vec{S}_j + B_{\text{ext}} \sum S_{iz},$$

where  $J_{01} > 0$  is the NN and  $J_{02} < 0$  the SNN exchange parameters, respectively. For the bulk SC lattice,  $\alpha = 6$  and  $\beta = 12$ . The transition temperature in the bulk systems in the mean field approximation (MFA) for Heisenberg model is proportional to the on-site effective exchange parameter  $J_0 = \Sigma J_{0j}$ .  $J_0$  for the particle interior is the same as for the bulk system  $J_0^{\text{interior}} = 6J_{01} + 12J_{02}$ . In our model nanoparticle, the lattice is truncated by eight (1 1 1) planes and six (0 0 1) planes forming a TO. The atoms on the (1 1 1) surface have three NN and nine SNN, and  $J_0^{(111)} = 3J_{01} + 9J_{02}$ . The magnetic interactions at the surface and interior of the nanoparticle can be drastically different depending on the ratio  $R = J_{02}/J_{01}$ . For example, for  $R = -1/3$ ,  $J_0^{\text{interior}} = 2J_{01}$ , while  $J_0^{(111)} = 0$ . It means that in the MFA the surface by itself should not have FM order even at  $T = 0$ . Furthermore, TO has sharp edges and vertexes which have even larger ratio between numbers of SNN to the numbers of NN. For example, NN/SNN = 7/2 for the edge sites, making these sites nucleation points for surface magnetic disorder.

The strong exchange coupling with the particle interior would normally prevent a separate surface transition temperature. For the system with competing interactions, however, the effective exchange coupling between the surface and interior is reduced significantly. The ratio  $R$  controls the exchange interactions between the surface and the subsurface layers giving possibility of decoupling between surface and bulk ordering temperatures. For example, the outermost (1 1 1) surface of our model particle will have negative coupling with the second layer, and positive coupling with the third layer making effective coupling of the surface layer to the bulk very weak. Note that no modified surface-to-bulk exchange parameters are introduced, and the decoupling of surface layer occurs due to the symmetry of surface termination. The surface magnetic excitation in this case effectively decouples from the bulk, and modifies the temperature dependence of the total magnetization below the surface order temperature upon cooling.

TOs with different numbers of atoms are configured to mimic nanoparticles from 3 to 5 nm in size. Shown in figure 1 is a schematic of a 1297 atom particle. MFA is not applicable for small finite systems; we use Monte Carlo (MC) method with Metropolis algorithm to calculate the total magnetization and magnetic susceptibility as functions of temperature [15]<sup>5</sup>.  $R$  ratio is varied from  $-0.3$  to  $-0.1$ . We find that low temperature magnetization is *very sensitive* to  $R$ . We obtain a net magnetization close to zero at  $T = 0$  for  $R = -0.3$ . Figure 2 shows that at  $R = -0.22$ , the particle is FM at

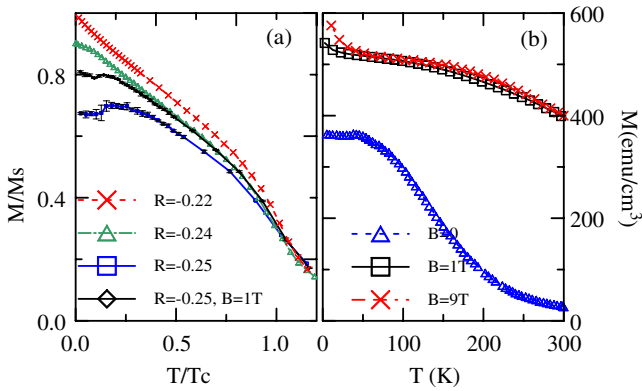


**Figure 1.** Model nanoparticle containing 1297 sites. Arrows show a near zero temperature structure for 1297-site nanoparticle with  $R = -0.24$ . Magnetic moments of the (1 0 0) faces (red) align themselves at the angle (near 45° clockwise) with magnetization of core sites and at near 90° with spins of sites in (1 1 1) faces. (Colour online.)

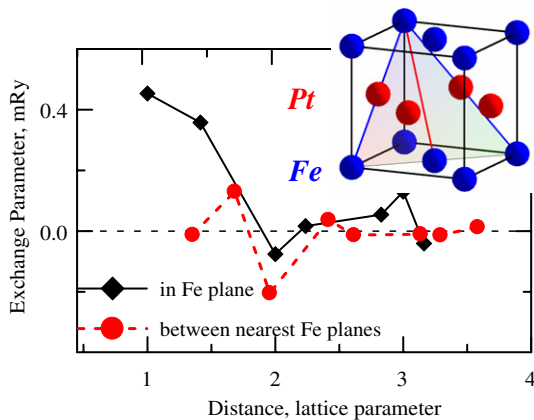
$T = 0$ , which corresponds to all spins aligned in the same direction. At  $R = -0.24$ , the surface spins become non-collinear at  $T = 0$  (figure 1). This leads to the reduction of total magnetization at  $T = 0$ . The reduction is more prominent for more negative  $R$  values, as can be seen from the systematic change of  $M(T = 0)$  for  $R = -0.22$  to  $-0.25$ . The effect is also stronger for smaller particles due to the increased surface-to-volume ratio. Our simulation indicates that at  $R = -0.24$ , 95% of the bulk  $M_s$  is retained at  $T = 0$  for a 3825 atom particle, as compared with 90% for the 1297 atom particle.

A striking difference between the nanoparticle and bulk behaviour is that for nanoparticles the magnetization exhibits a strong deviation from the Bloch's  $T^{3/2}$  law at low temperatures. The experimental data for remanent magnetization shows plateau, while in strong magnetic field it has an exponential upturn. Theoretical curves also show specific temperatures at which magnetization behaviour abruptly changes. The physical origin of such behaviour is a separate ordering temperature for the surface, above which surface spins are not contributing substantially to the total magnetization. Below the ordering temperature the surface layer acquires the magnetization which is either in the same direction as the inner part (at  $R = -0.22$ ), effectively increasing total magnetization; or forms a non-collinear structure, effectively reducing the magnetization (at  $R < -0.24$ ). The magnetization significantly increases in an applied field and a slight magnetization upturn is observed as the temperature decreases below the surface ordering temperature. However, the comparison of this curve with experimental data is only qualitative because Monte Carlo method with Metropolis algorithm does not include magnon excitations which are dominant at low temperatures. The increase in the fluctuation (shown by the error bars in figure 2(a)) at low temperatures indicates the presence of multiple states with similar energies but different magnetization resembling a paramagnetic behaviour. Note that the freezing of the surface spins is not a necessary condition for such an upturn. If the

<sup>5</sup> We performed thermal averaging with  $6 \times 10^6$  MC steps which we repeated 4 times to find a statistical error.



**Figure 2.** (a) Simulated magnetization as a function of temperature for various ratio  $R$  for a 1297 atom particle with SC lattice; (b) measured  $M_s$  as a function of temperature for 3 nm FePt nanoparticles in the applied field of up to 9 T. (Colour online.)



**Figure 3.** Pair exchange interaction parameters between Fe sites in FePt. Unit is  $a/\sqrt{2}$ . The insert shows a schematic of the unit cell of  $L_{10}$  structured FePt. The circles represent FM exchange between SNNs and diamonds show AFM exchange between 3NNs. (Colour online.)

surface (or part of the particle) remains paramagnetic at low temperatures [2] it will be sensitive to an external field. In this case the surface magnetization behaves as a Langevin function (approximately as  $B/T$ ). Besides the exchange interaction the magnetic behaviour of the nanoparticle and its size dependence is strongly affected in many cases by the surface anisotropy [16].

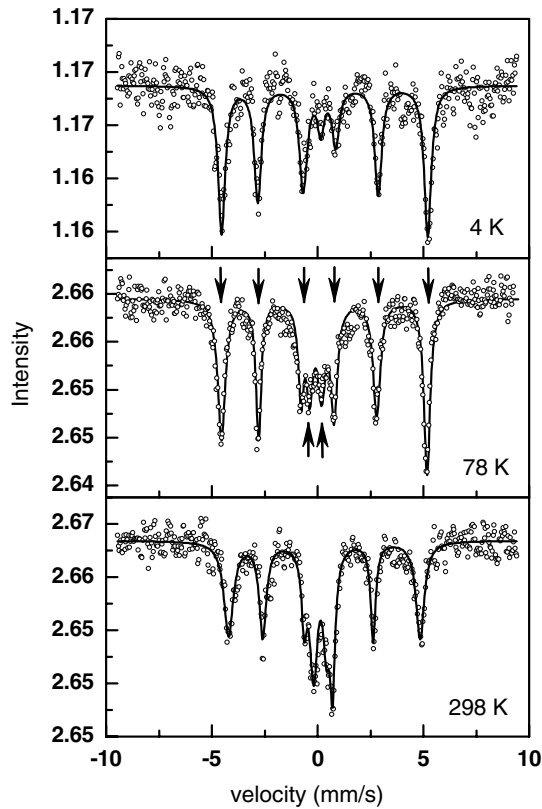
The basic concept of the effect of symmetry modification at the surface is demonstrated here using SC lattice. Other lattices should exhibit similar sensitivity to a ratio of competing exchange interactions. For example, *fcc* lattice has 12 NN and six NNN. For the particle with the shape of TO, which is terminated by (100) and (111) planes, we find (using direct MC calculations) that the ratio at which instability of magnetization occurs is  $R \sim -1.04$  (because (100) plane has four NN and four NNN). Thus, the general physics is applicable to other systems with *fcc*, tetragonal, or *bcc* lattices. The necessary condition for observing above effects is the presence of AFM interactions which contribute stronger at the surface

than in the interior of the nanoparticle. This is a common feature in Fe-based compounds [10, 17].

We next focus on FePt nanoparticles, due to their technological relevance to future data storage applications.  $L_{10}$  ordered FePt alloy possesses tetragonal structure shown schematically in figure 3. It has layered structure and complex exchange interactions, with pair exchange interactions in the Fe-plane ((001) plane) being strongly FM, while interactions between the planes being much weaker. We have performed first-principle calculations of the exchange interactions as a function of interatomic spacing for Fe–Fe pairs both in the (001) plane and inter-plane [15]. It is shown in figure 3 that the in-plane Fe–Fe pair exchange interactions are FM for both NN and SNN. Inter-plane Fe–Fe pair exchange interactions are close to zero for the NN, FM for SNN and AFM for the third nearest neighbour (3 NN). The latter exchange parameter is the largest in magnitude and gives overall negative Fe–Fe inter-plane interactions. This is offset by contributions from the itinerant Pt sites to render FM properties of bulk FePt [18].

Because of the missing neighbouring atoms and competing interactions, the surface magnetic order is significantly altered, depending on surface terminations. For the (100) surface, each Fe atom has two in-plane SNN with  $J_{ij} > 0$  (FM exchange interactions), two inter-plane NN with  $J_{ij} \approx 0$  and four inter-plane 3NN with  $J_{ij} < 0$ . As a result the overall interactions at the surface would look like AFM coupled FM chains. This is a 2D plane with zero magnetization, i.e. a ‘dead layer’ even at zero temperature. Similarly (111) termination has two in-plane NN, two inter-plane NN and four inter-plane 3NN. This facet also resembles AFM coupled FM chains. The (001) facet, on the other hand, is FM, with each atom having four in-plane NN and four in-plane SNN, both of which exhibit FM interactions. The (110) facet is also FM, with each atom having two in-plane NN, two inter-plane NN and four inter-plane SNN. Direct MC calculations show that critical ratio between exchange of 3NN and SNN at which magnetization of the TO particle reduces to about 70% of the bulk is  $R \sim -0.55$ . The transition from ferromagnetic to non-collinear structure as a function of  $R$  occurs in very narrow region from  $R = -0.51$  to  $R = -0.58$  similar to other lattices. This ratio is very close to one expected in FePt.

Monodisperse  $L_{10}$  structured FePt nanoparticles with tunable sizes were realized experimentally by annealing as-synthesized nanoparticles in NaCl matrix [3]. The annealing also removed the surfactants and reduced the surface oxides. X-ray diffraction shows high  $L_{10}$  ordering, with no secondary phase detected. HRTEM shows that nanoparticles are single crystals with two main shapes: TO and cubic [3, 14]. TO octahedron is dominated by (111) and (100) facets, with only small fraction of (001) facets. The mainly cubic particles are dominated by (100) facets at the sides and (111) at the corners, with (001) facets only at the top and bottom. Since both (111) and (100) facets prefer AFM order, effects similar to those discussed for the model nanoparticle, namely reduced magnetization at  $T = 0$ , ‘dead layer’ at finite temperatures, and unconventional temperature dependence of magnetization should be expected.



**Figure 4.** The Mössbauer spectra of 4 nm FePt nanoparticles measured at three different temperatures. The spectra represent transmission (counts) versus velocity ( $\text{mm s}^{-1}$ ) obtained by the source,  $^{57}\text{Co}(\text{Rh})$ , versus the absorber, 4 nm PtFe, at different temperatures. The dots are the data and the lines are the superposition of all the line fits to the data. The six down arrows represent the ferromagnetic sextet and the two up arrows represent the paramagnetic doublet.

$^{57}\text{Fe}$  Mössbauer spectrum measured at 298 K shows two Fe species: a FM sextant and a paramagnetic doublet, as shown in figure 4(a). The hyperfine field of the sextant is around 30 T, consistent with previously reported results for  $L1_0$  FePt [19]. The doublet indicates that a significant fraction of the Fe atoms is not ferromagnetic at 298 K. When cooled to 4 K, no new sextant appears. Rather, the intensity ratio of the doublet to sextant is drastically reduced (figure 4(c)). This suggests that the doublet does not belong to another iron phase, but rather is a result of disordered surface spins behaving paramagnetically. At  $T = 4$  K, the doublet feature still persists, which is consistent with our model prediction that there is a magnetically disordered surface even at  $T = 0$ . At  $T = 298$  K, the whole surface becomes paramagnetic, due to its lower ordering temperature. An observation of the 78 K spectra is particularly noteworthy because in it the paramagnetic doublet component is clearly resolved from the ferromagnetic sextet component as shown by the arrows in the spectra (figure 4(b)). The Mössbauer parameters ( $IS$ ,  $E_Q$ ,  $\Gamma_{AV}$ ) for the spectra in figure 4 are shown in table 1, which are very consistent for all the temperatures considering the noise in the spectra due to the small size of the 4 nm particles. The area ratio

of the ferromagnetic sextet to paramagnetic doublet changes approximately as 3 : 1 (298 K); 4 : 1 (78 K); 10 : 1 (4.2 K) as the temperature is lowered. This shows that there is still some paramagnetic component at 4.2 K as predicted in our model.

Magnetization (measured at 0, 1 and 9 T) as a function of temperature for 3 nm FePt is shown in figure 2(b). Overall, the magnetization shows much stronger temperature dependence than that of bulk. This can be understood since the surface magnetic structure reduces the overall FM exchange, and is also consistent with the simulation results. 4 K magnetization measured at 9 T is less than half of the bulk  $M_s$ . This is consistent with our simulation showing magnetization lower than the bulk  $M_s$  at  $T = 0$ , primarily due to preferred non-collinear order at surfaces. Since for a 3 nm particle, more than 50% of the atoms are at the particle surface, this should lead to reduction of the magnetization by more than 50%. Recent magnetic circular dichroism studies also show reduction of magnetic moment by 15–30% in individual free FePt nanoparticles of 6–7 nm in diameter [5]. Magnetization behaviour is qualitatively different with and without field: at  $H = 0$ , magnetization stops increasing at about 50 K, and slightly decreases with further decreasing temperature; for  $H = 9$  T, the increase in magnetization is slower from 150 to 25 K than at higher temperatures. However, an upturn is observed as the temperature is decreased below 25 K. The qualitative agreement between simulation and experimental results can be clearly see from figure 2, although the simulation is done on a SC model nanoparticle and direct quantitative comparison with experiment cannot be made.

We have chosen the essential ingredient, i.e. competing interactions, to model the magnetization reduction in nanoparticles. Other factors could also influence the magnetization of nanoparticles. Defects such as vacancies will lead to similar effects to surface atoms with missing neighbours and broken exchange bonds. Surface atomic environment can be somewhat different from that of interior of the particle. Fe atomic moment can be enhanced to as high as  $3\mu_B$  at the surface. Possible formation of  $\text{Fe}_3\text{C}$  or iron oxides will reduce the surface Fe moment. This change should play a minor role in surface magnetization<sup>6</sup>.

In conclusion, we have shown that strong reduction of magnetization in nanoparticles is an intrinsic effect for materials with competing interactions. This model is based purely on geometrical constraints: broken symmetry and missing nearest neighbours leading to preferential AFM order for certain surface terminations. The predictions of an unconventional temperature dependence of magnetization and existence of a magnetically ‘dead layer’ are consistent with experimental results. The outcome has strong implications in future applications of magnetic nanoparticles for bio-medical and data storage fields.

<sup>6</sup> Our elemental analysis on similar samples shows that carbon content is less than 1 at%. The Mössbauer spectrum puts the second phase upper limit at about 5%, limited by its noise level. The presence of oxides does not change the qualitative picture of the magnetic interactions and its effect on total magnetization because it effectively introduces AFM superexchange coupling in the surface layer.

**Table 1.**  $^{57}\text{Fe}$  Mossbauer Spectra Parameters for PtFe 4 nm Particles.  $\Gamma_{\text{AV}}$  is the average line width, IS is an isomer shift,  $E_Q$  is an electric quadruple splitting, H is a hyperfine field.

Temperature (K)		$\Gamma_{\text{AV}}$ (mm s $^{-1}$ )	IS (mm s $^{-1}$ )	$E_Q$ (mm s $^{-1}$ )	H (T)
4.2K	Ferromagnetic component	0.40(.04)	-0.14(.04)	0.32(.04)	30.2(0.6)
	Paramagnetic component	0.40(.04)	0.20(.04)	0.71(.04)	
78K	Ferromagnetic component	0.37 (.04)	-0.11(.04)	0.31(.04)	30.2(0.6)
	Paramagnetic component	0.37(.04)	0.09(.04)	0.56(.04)	
298K	Ferromagnetic component	0.44 (.04)	-0.13(.04)	0.30(.04)	27.6(0.6)
	Paramagnetic component	0.11 (.04)	0.60(.04)	0.4(.04)	

## Acknowledgment

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