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# Monte Carlo simulation of equilibrium $L1_0$ ordering in FePt nanoparticles

R. V. Chepulskii[a)]
*Center for Materials for Information Technology, University of Alabama, Box 870209, Tuscaloosa, Alabama 35487-0209 and Department of Solid State Theory, Institute for Metal Physics, National Academy of Sciences of Ukraine (NASU), Vernadsky 36, Kyiv-142, UA-03680, Ukraine*

J. Velev and W. H. Butler
*Center for Materials for Information Technology, University of Alabama, Box 870209, Tuscaloosa, Alabama 35487-0209*

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First, second, and third nearest-neighbor mixing potentials for FePt alloys were calculated from first principles using the Connolly–Williams approach. Using the mixing potentials obtained in this manner, the dependency of equilibrium $L1_0$ ordering on temperature was studied for bulk and for a spherical nanoparticle with a 3.5-nm diameter at equiatomic composition by use of Monte Carlo simulation and the analytical ring approximation. The calculated order-disorder temperature for bulk (1495–1514 K) was in relatively good agreement (4% error) with the experimental value (1572 K). For nanoparticles of finite size, the (long-range) order parameter changed continuously from unity to zero with increasing temperature. Rather than a discontinuity indicative of a phase-transition we obtained an inflection point in the order as a function of temperature. This inflection point occurred at a temperature below the bulk phase-transition temperature and which decreased as the particle size decreased. Our calculations predict that 3.5-nm diameter particles in configurational equilibrium at 600 °C (a typical annealing temperature for promoting $L1_0$ ordering) have an $L1_0$ order parameter of 0.83 (compared to a maximum possible value equal to unity). According to our investigations, the experimental absence of a (relatively) high $L1_0$ order in 3.5-nm diameter nanoparticles annealed at 600 °C or below is primarily a problem of *kinetics* rather than equilibrium. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1852351]

## I. INTRODUCTION

Self-assembled, monodispersed FePt nanoparticles are being intensively investigated for possible future application as an ultrahigh-density magnetic storage medium. In order to be useful as a storage medium, these particles, because of their extremely small volume $V$ must have sufficiently high magnetic anisotropy $K_u$ to withstand thermal fluctuations of the direction of magnetization. This requires values of the thermal stability factor, $(K_uV)/(k_BT)$, of approximately 50. The particles are usually produced by a "hot soap" process that yields a disordered fcc solid solution alloy (e.g., Ref. 1). Such particles are not useful for information storage because they are superparamagnetic at room temperature due to their low magnetic anisotropy.

Typically, the particles are annealed at a temperature $T \simeq 600$ °C in order to induce an ordered $L1_0$ phase.[2,3] The layered $L1_0$ phase[4] is known from studies of bulk alloys to have an extremely high magnetic anisotropy ($K_u \cong 7 \times 10^7$ ergs/cm$^3$). This value of magnetic anisotropy would provide a sufficiently large thermal stability factor to make 3.5-nm diameter particles viable for information storage.

Unfortunately, it appears to be difficult to a achieve a high degree of long-range atomic order in FePt *nanoparticles* with $\lesssim$4-nm diameter by annealing at $T \lesssim 600$ °C (e.g., Ref. 2). One can consider two possible reasons for the fact that it has not been possible to obtain well-ordered small particles. First, the observed order may be low because the particle is *not* in its equilibrium state due to the slow kinetics at low temperatures. Alternatively, the *equilibrium* order itself may be low even at relatively low temperatures because of the small size of the nanoparticles. The latter explanation was suggested in Ref. 2. There, the order-disorder phase-transition temperature was estimated to decrease with decrease of particle size. For particle sizes less than 1.5 nm in diameter, the phase-transition temperature was found to be below the typical annealing $T \simeq 600$ °C. Therefore, particles of diameter less than 1.5 nm were predicted to have no long-range order in their equilibrium state at 600 °C. This explanation is in qualitative agreement with the experiment. The difference between the experimental (4 nm) and theoretical (1.5 nm) critical sizes for disappearance of $L1_0$ order at 600 °C was attributed to the neglect of nanoparticle surface effects.

From our point of view, however, the results obtained in Ref. 2 require verification because of the limitations of the theoretical models used in that study. Namely, the interatomic potentials in alloys usually are much more complicated and long ranged than the nearest-neighbor Lennard-Jones model that was used. In addition, the order-disorder phase-transition temperature was estimated in Ref. 2 by comparing the free energies of completely ordered and completely disordered states; whereas in reality, the ordered state approaches (with increasing temperature) the phase-transition point being not completely ordered. Also, the disordered state would be expected to approach the phase tran-

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[a)] Electronic mail: r_chepulskii@yahoo.com sition (with decreasing temperature), not with a completely random atomic distribution but with an atomic distribution that has substantial short-range order. Moreover, it is known[5] that there is no formal phase transition in a finite system.

In the present paper we utilize first-principles calculations (VASP code[6]) together with the Connolly–Williams[7] method and Monte Carlo (MC) simulations (utilizing the Metropolis algorithm[8] ) to study the temperature dependence of equilibrium $L1_0$ order in a spherical FePt nanoparticle with 3.5-nm diameter and equiatomic composition ($c=0.5$).

## II. RESULTS

We consider an Fe–Pt alloy in the framework of the commonly used two-component lattice-gas model. In such a model,[9] two types of atoms are distributed over the sites of a rigid crystal lattice. The atoms are allowed to be situated only at the crystal lattice sites and each site can be occupied by only one atom. The atoms interact through the lattice potentials (the so-called mixing potentials) and can exchange their positions according to Gibbs statistics.

We used the Connolly–Williams[7] method to calculate the mixing potentials. Within this method, the energies of several periodic atomic distributions (i.e., long-range-ordered structures called superstructures; for example, $L1_0$) are calculated by first-principles methods. Then the mixing potentials are determined by the best fit to those energies. We considered 23 linearly independent Fe–Pt superstructures of the same equiatomic composition $c=0.5$. First-principles calculations were performed within the local-density approximation to density-functional theory, using the VASP program package.[6] All superstructures were totally relaxed including shape and volume relaxation of the unit cell and individual displacements of atoms within the unit cell. An $8\times8\times8$ mesh of $k$ points in the full Brillouin zone was employed.

The $L1_0$ superstructure was included in our first set of first-principles calculations. In this case, after atom position relaxation, we obtained 3.848 and 3.771 Å for $a$ and $c$ lattice parameters of the corresponding tetragonal lattice, respectively. For comparison the experimental values are 3.847 and 3.715 Å.[10] In addition, our calculated results showed the $L1_0$ ferromagnetic superstructure to be more stable (i.e., has lower energy) than the antiferromagnetic one in accordance with the experiment. We believe that this good correspondence between theoretical and experimental results confirms the adequacy of our VASP first-principles calculations.

By applying the Connolly–Williams method, we obtained 0.087 69, −0.039 46, and 0.015 85 eV for the first, second, and third nearest-neighbor pair mixing potentials, respectively. The average accuracy with which we fit the energy of the 23 superstructures within the Connolly–Williams method was 1.14% per one structure.

To verify the calculated values of mixing potential, we calculated the phase-transition temperature in the *bulk* FePt alloy using these values. As a result we obtained 1495 and 1514 K within the analytical ring approximation[11] and MC simulation, respectively. The close correspondence of these values to the experimental[12] one of 1572 K (4% error), demonstrates the adequacy of the calculated mixing potential.

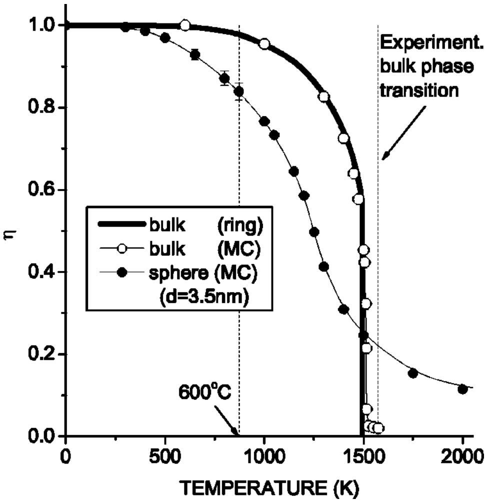

FIG. 1. The temperature dependence of the FePt equilibrium $L1_0$ order parameter $\eta$ in the cases of bulk ("bulk") and a spherical nanoparticle with 3.5-nm diameter ("sphere") at equiatomic composition $c=0.5$. Two results for bulk were obtained by Monte Carlo simulation ("MC") for parallelepiped sample containing $N=216\,000$ atoms and within the analytical ring approximation[11] ("ring"). At simulation, the starting configuration for each temperature was chosen to be the completely ordered one. We applied free and periodic boundary conditions in cases of spherical nanoparticle and parallelepiped, respectively. For the case of a nanoparticle at 378, 528, and 600 °C, the error bars correspond to dispersion of $\eta$ due to the thermodynamic fluctuations.

To investigate long-range order in spherical nanoparticles, we used the calculated mixing potentials in MC simulations to determine the temperature dependence of the equilibrium $L1_0$ order parameter $\eta$ in the case of spherical FePt nanoparticles with 3.5-nm diameter and equiatomic composition $c=0.5$. The results are presented in Fig. 1.

We define the equilibrium $L1_0$ order parameter $\eta$ as the statistical average of the maximum value among three absolute values of "directional" order parameters $\eta_x$, $\eta_y$, and $\eta_z$:

$$\eta=\langle\max\{|\eta_x|,|\eta_y|,|\eta_z|\}\rangle_{\mathrm{MC}}, \tag{1}$$

where $\eta_i(i=x,y,z)$ is defined as the difference between the Fe atom concentrations at odd and even crystal planes perpendicular to $i$th direction, and $\langle\ldots\rangle_{\mathrm{MC}}$ is the statistical average over the MC steps. We chose such a definition of $\eta$ because of the equivalence by symmetry of the $x$, $y$, and $z$ directions of $L1_0$ order. In addition, one can obtain an equivalent structure (at $c=0.5$) by changing the sign of $\eta_i$, which results in the exchange of Fe and Pt atoms producing a configuration that is equivalent by symmetry to the original one. During MC simulation, we observed fluctuations that cause transformations between these equivalent states (i.e., fluctuations in the sign and direction of $\eta$).[13] This is in addition to the usual statistical fluctuations within one such state. The $L1_0$ order parameter $\eta$, defined in Eq. (1), takes into account the fluctuation induced transformations between the equivalent states.[15]

## III. CONCLUSIONS AND DISCUSSION

From Fig. 1 one may conclude the following. The ring approximation (which corresponds to bulk, i.e., an infinite sample) clearly shows a phase transition when the order parameter $\eta$ drops to zero. Strictly speaking, in both of the cases considered here of finite-size samples (sphere and parallelepiped) there is no phase transition in accordance with a general theorem.[5] The order parameter $\eta$ continuously changes from unity to zero with increasing temperature and instead of a phase transition we obtain an inflection point in the $\eta(T)$ curve. In the case of the parallelepiped with 216 000 atoms, the inflection point is very similar to the phase transition.[16]

Our calculations predict that 3.5-nm diameter particles in configurational equilibrium at 600 °C would have an order parameter $\eta=0.83$ (compared to a maximum possible value of unity). Therefore, annealing at 600 °C will not yield a perfect order for 3.5-nm diameter particles. Approximately 17% of the atoms will be on the wrong sublattices, even in equilibrium. The dispersion of $\eta$ due to the thermodynamic fluctuations is comparatively small (2.5%) near annealing $T=600$ °C.

According to our investigations, the experimental absence of (relatively) high order in nanoparticles below 600 °C is primarily a *kinetic* problem rather than an equilibrium one. It should be noted that to rapidly obtain the correct equilibrium state, we used simplified kinetics in our MC simulation.[17] Namely, we allowed *any* two randomly chosen atoms to exchange their positions *without* an additional diffusion barrier. In a real alloy, the main mechanism of atomic diffusion is much slower because it consists in exchange the positions between atoms and their nearest-neighbor vacancies through energy barriers. Moreover, at each temperature we started the simulation from the completely ordered state, whereas the actual nanoparticles are initially prepared in the disordered state and transformation from the disordered to the ordered state may be much slower than the reverse one, especially at low temperatures. Nevertheless, even with our simplified kinetics, we observed a slowing down problem in approaching the equilibrium ordered state at low temperatures. In real nanoparticles this problem must be much worse. Kinetic acceleration methods such as irradiation and/or addition of other types of atoms[18] may be useful in accelerating the formation of long-range order.

In our study we used mixing potentials obtained for *infinite* bulk alloys and used *free* boundary conditions to simulate the equilibrium configuration of finite-size particles. The presence of the surface will change the atomic potentials in the near-surface region in comparison with bulk potentials. Analytical estimation of such surface effects is not straightforward and will be done elsewhere.[14] In reality, the problem of the effect of the surface on the interatomic exchange potentials is even more complicated because the nanoparticles of most current interests are likely to have unknown atoms and molecules attached to their surfaces.

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[13] We did not observe the antiphase domains and in Ref. 14 it will be shown that they are not favored energetically.
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[15] Because of the above-discussed symmetry equivalence, we obtain $\langle\eta_i\rangle_{\mathrm{MC}}=0$ for any $i=x, y, z$ at *any* temperature when the statistical average is taken over a sufficiently large number of MC steps.
[16] Often the inflection point is used to approximate the bulk phase transition point in MC simulations of finite-size samples.
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