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Observation of $L1_0$-like chemical ordering in a decahedral FePt nanoparticle by C_s-corrected high resolution transmission electron microscopy

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The state of the chemical ordering in a decahedral FePt nanoparticle was studied using aberration corrected high resolution transmission electron microscopy. With the reduced image delocalization effect as a result of spherical aberration correction, it is possible to directly correlate the image intensity with the local state of chemical ordering through the help of a multislice image simulation. We have found direct evidence for the image intensity oscillation from one atomic layer to another. It is interpreted as $L1_0$-like chemical ordering, i.e., the alternate occupation of Fe and Pt atoms in the (002) planes. The result suggests that chemical ordering survives even in decahedral nanoparticles down to 3 nm size despite the possible surface effects. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3068407]

I. INTRODUCTION

Chemically ordered binary alloy $L1_0$-FePt has stimulated a great research interest during the last few years. Because of its ultrahigh uniaxial magnetocrystalline anisotropy and good chemical stability $L1_0$-FePt is promising as a ultrahigh density magnetic recording media material.[1,2] FePt alloys with near equal-atomic composition have two phases with one chemically ordered ferromagnetic $L1_0$ phase and the other a disordered face-centered-cubic (fcc) phase.[3] The magnetic properties depend greatly on the degree of chemical order in the $L1_0$ phase.[4–7] However, FePt nanoparticles produced from room temperature sputtering and chemical synthesis process normally are in the disordered fcc phase and postsynthesis treatments are necessary to induce the phase transformation to the ordered $L1_0$ phase. Most postsynthesis treatments, such as thermal annealing, also lead to aggregation of the nanoparticles. This has prevented a meaningful experimental study on the phase transformation and magnetic properties of the nanoparticles as a function of the particle sizes. One of the exceptions is the coannealing method in a ground salt matrix[8,9] and strong size dependent magnetic properties have been observed as a result.[10] Size dependence in chemical ordering of FePt nanoparticles has been observed.[10–19] Theoretical simulation suggests that this size dependence may result from a strong surface effect in small particles.[15–18,20–23] Until now, this is either studied on an ensemble basis using x-ray diffraction to measure the macroscopic averaged ordering parameters[24] or on an individual particle basis using electron diffraction to obtain a particle averaged ordering parameters.[25,26] It is however desirable to study the state of the chemical ordering in small FePt nanoparticles in real space with high spatial resolution.

High resolution transmission electron microscopy (HRTEM) is capable of imaging crystal lattices with very high spatial resolution and becomes a powerful tool for studying nanostructured materials.[27] Especially with the help of the newly developed lens spherical aberration corrector (or C_s-corrector),[28] not only the spatial resolution of the HRTEM can be greatly improved but also the delocalization effect of the HRTEM images can be greatly reduced.[29] These make it possible for a close match of the detailed image characteristics with the local atomic structures. Here we report our study on a decahedral FePt nanoparticle using the C_s-corrected HRTEM technique. The intensity oscillation of the image reflects the local ordering state of the particle from the particle core to the edge in a layer-resolved manner. This high spatial resolution analysis of the ordering state of $L1_0$-FePt will benefit the understanding of the structure and magnetic-property relationships of small ferromagnetic nanoparticles.

II. EXPERIMENTS AND RESULTS

FePt nanoparticles with the fcc structure were synthesized using a wet chemical approach similar to Sun and co-workers.[1,30,31] The as-synthesized nanoparticles were then buried in finely ground salt matrix and annealed at temperatures above 700 °C. This salt-matrix annealing technique can produce ordered $L1_0$-FePt nanoparticles without aggregation.[8,9] The annealed nanoparticles were washed, dispersed in isopropanol, and fished out with a carbon coated transmission electron microscopy (TEM) grid. TEM experiments were carried out on a JEOL-2200FS TEM with a field emission gun operating at 200 kV. This TEM was equipped

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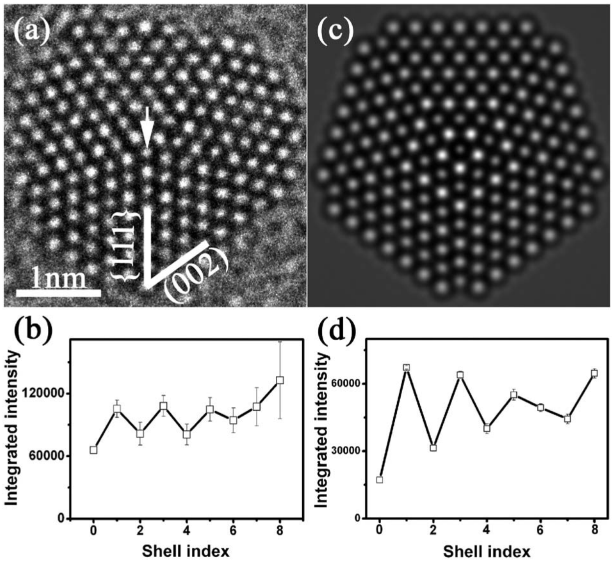

FIG. 1. (a) C_s-corrected HRTEM image of a FePt decahedron. (b) Averaged atom column intensities as a function of shell index where 0 stands for the central atom column. (c) Simulated HRTEM image of an ordered D15 Marks decahedron particle. (d) Simulated atom column intensities as a function of shell index.

with C_s-correctors for both condenser and objective lens. This work uses only the corrector for the objective lens.

The starting nanoparticles have an average size of 4 nm and a narrow size distribution with the standard deviation less than 0.4 nm. After the salt matrix annealing, the particle size distribution does not appear to change. Most of the nanoparticles are single crystals with no sign of defects. Occasionally, smaller than average nanoparticles are detected with twinned structures. Multiply twinned nanoparticles are even rarer and only found in small sizes. Their small size means that they are important to test the possible size dependence in the stability of the chemically ordered state. Figure 1(a) is a HRTEM image of a decahedral FePt nanoparticle viewed along its fivefold axis. The image was taken with the C_s of the objective lens adjusted to a nominal value of 1.42 μm and the supporting carbon film was imaged at an over-focus value of about 10 nm. In this orientation, the decahedron was composed of eight shells of (002) atom planes surrounding a central atom column, which was indicated by a white arrow in Fig. 1(a). In order to quantitatively analyze the image intensity variations, each image of the atom column was fitted with a Gaussian function. To reduce the background contribution from the amorphous carbon support, the integrated intensities of the Gaussians for the atom columns in the same shell were averaged. Figure 1(b) shows the averaged intensities for each shell from the central atom column to the decahedron edge as a function of the shell index. Oscillatory behavior is observed with a periodicity of two (002) atomic layers.

We have taken the oscillatory behavior as a sign for the $L1_0$-like chemical ordering in the decahedral nanoparticle, as Fe and Pt atoms occupy (002) planes alternatively in an ordered $L1_0$-FePt phase. To confirm this, we have carried out an extensive multislice image simulation to study the image contrast as a function of chemical ordering as well as imaging conditions. We have focused on six possible decahedrons:[32] (i) the regular complete decahedron which contains nine atoms in the central column (D9), (ii) the regular complete decahedron which contains ten atoms in the central column (D10), (iii) the Marks decahedron which contains 15 atoms in the central column, eight atom columns along the twin boundary, and eight (002) planes along the [002] direction (D15), (iv) the Marks decahedron which contains 17 atoms along the central column, nine atom columns along the twin boundary, and nine (002) planes along the [002] direction (D17M), (v) the Ino decahedron which contains 17 atoms in the central column and nine atom columns along the twin boundary (D17I), and (vi) the Ino decahedron which contains 19 atoms in the central atom columns and ten atoms along the twin boundary (D19I). All six decahedrons have similar cross sectional projections that are consistent with the highest possible symmetry of the observed image. They are distinguished by the different atomic column heights along the viewing direction.

HRTEM images were simulated for each of the six structures near the axial orientation as a function of the imaging parameters using a multislice method.[33] The thermal effect has been taken into account by using the frozen lattice method. It was found from the multislice simulation that except for the D10 structure, the other five structures with $L1_0$-ordering can have HRTEM images similar to that shown in Fig. 1(a). Figure 1(c) is the simulated image for the ordered D15 structure and Fig. 1(d) is the image intensity similar to that shown in Fig. 1(b). The simulation results for the D9, the D17M, the D17I, and the D19I structures were found to be similar. We have also calculated the image contrast for similar nanoparticles but with a random atomic arrangement of Fe and Pt atoms and found that the oscillatory behavior is absent. This confirms the possibility of using the image contrast oscillation as a fingerprint to estimate the ordering state of the real particle. In fact, we can extend this analysis further to find out the local state of chemical ordering in an atomic layer resolved manner. From Fig. 1(b) we can find that the image intensity oscillated for the inner five shells while it is not obvious in the outer three shells. This means that Fe and Pt ordered on the (002) planes at least for the five inner shells. The situation for the outer three shells is unclear. Further work is required both to quantitatively define and determine the local chemical order parameter in nanoparticles and to identify the nature of the surface atomic structure.

III. DISCUSSIONS

HRTEM studies of decahedral FePt nanoparticles have already been reported previously.[34–37] However due to the significant image delocalization and complicated relationship between image intensity and the imaging parameters for conventional HRTEM no detailed analysis has been attempted with high spatial resolution and our result represents the first attempt to correlate the chemical ordering of FePt with the image intensities in a layer-resolved manner.

Our result suggests that multiply twinned FePt nanoparticles can still be ordered in a thermally equilibrated thermal environment with its diameter as small as 3.4 nm. This kind of ordering state for cyclic twinned FePt nanoparticles has been discussed in theoretical simulation[38] but it has never been experimentally identified before. Our result means that the magnetocrystalline anisotropy of the single crystalline domain in such a nanoparticle may retain a value close to that found for bulk materials but the magnetocrystalline anisotropy may be very small as the five single crystalline parts are oriented differently.

IV. CONCLUSIONS

The state of chemical order in a 3.4 nm decahedral FePt nanoparticle was studied using C_s-corrected HRTEM. Multislice image simulation results indicate that the ordering along [002] directions will result in the observed image intensity oscillating between two successive shells. We therefore conclude that the five inner shells of this decahedral nanoparticle were in a chemically ordered state and the three outer shells may be in a relatively lower ordered or disordered state. This layer-resolved analysis of the ordering state will result in a better understanding of the size dependent magnetic properties for small FePt particles.

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