doi:10.1017/S1431927611003473
Microsc. Microanal. 17 (Suppl 2), 2011

Aberration-Corrected STEM Imaging and *In Situ* Heating Experiments on Stable Colloidal Solutions of FePt Nanoparticles

Maxime J-F Guinel,* Lawrence F. Allard,** Anastasia Delattre*** and Peter Reiss***

*Departments of Physics and Chemistry, Faculty of Natural Sciences, University of Puerto Rico, PO Box 70377, San Juan, Puerto Rico 00936-8377
**Materials Science and Tech. Div., Oak Ridge National Laboratory, Oak Ridge, TN 37831
***Institut Nanosciences et Cryogénie SPrAM (UMR 5819)/LEMOH, CEA-Grenoble, 17 Rue des Martyrs, 38054 Grenoble, France

Considerations of data transfer speeds and energy consumption drive the thrust to developing the next-generation data storage media with tremendously higher recording densities (on the order of terabytes per square inch). Self-assembled monolayers of FePt nanoparticles (NP) in their $L1_0$ ordered phase, in which Fe and Pt atoms alternate in layers along the c-direction of the tetragonal cell, are promising candidates because they show high uniaxial magnetocrystalline anisotropy along their c-direction (7×10^6 J•m^{-3}). The goal is to produce large mechanically stable arrays of these particles where each would store a single bit of information. The first step is to produce suspensions of A1 (disordered) particles with very well controlled size, distribution and stoichiometry. The next step is to thermally anneal these particles so as to obtain the high-anisotropy $L1_0$ phase, at its highest near $Fe_{50}Pt_{50}$ because the tetragonality is maximized. This study focuses on near-equiatomic FePt alloyed NPs synthesized via a method [1] that is efficient for the preparation of stable colloidal suspensions. Aberration-corrected high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) using a JEOL JEM 2200FS with a CEOS corrector on the illuminating lenses was coupled with *in situ* heating experiments using the Aduro™ heating system manufactured by Protochips, Inc. It allows for heating and cooling at rates reaching 10^6 °C/s. Wittig, et al. have reported similar experiments [2], but they used FePt NPs synthesized via a different method.

Figure 1 shows a HAADF-STEM image of an array of FePt NPs *ex-situ* annealed at 700°C for 8 hrs in a salt matrix. The NPs, before annealing, have a mean size of 3.6 nm and a size distribution of 9%. Figure 2(a) shows a HAADF-STEM image taken at 400°C of a partially ordered NP that was subjected 24 min. at 400°C then 1 min. at 500°C and 55 minutes at 400°C. Figure 2(b) shows a HAADF-STEM image recorded at room temperature of a fully ordered NP that remained at up to 800°C for 20 min. The chemical order is evident from the difference in intensity, Z-contrast (^{26}Fe and ^{78}Pt), between two successive planes of atoms along the <100> direction. Cell parameters were measured to be approximately a = 3.84 Å (A1) and a = 3.85 Å and c = 3.71 Å ($L1_0$). Observations are in accordance with XRD powder diffraction data, with Végard's law and x-ray energy-dispersive spectrometry. The presence of crystallographic defects reduces the degree of chemical order and therefore the magnetic anisotropy. Defective particles were observed but remain relatively rare. An example is shown in figure 3 where a STEM image was recorded from a twinned NP, fully ordered on both sides; the NP remained at up to 650°C for 1h20m.

It is difficult to quantitatively assess the proportion of re-ordered particles using HR imaging because the orientation of the particle examined, its morphology and the possible existence of defects are critical in determining the re-order [3]. Only a limited set of low index zone axes can be used to unambiguously determine whether the NPs are $L1_0$ or A1. In the former case, they will display the characteristic alternating layers of Fe and Pt atoms. A large number of particles must therefore be examined. Moreover, there exists a critical size for the $L1_0$ phase transformation to be triggered; particles below 1.5 to 2.0nm in size were shown not to reorder [4]. The order parameter

actually drops sharply below 3.0 nm, and decreases to zero for NPs less than 2 nm. In this study, we are very close to this limit. Figure 4 shows HAADF-STEM images of three fully ordered NPs with very small sizes. The NPs (approx. 2.6 nm by 3.3 nm) shown in (a) and (b) remained at 650°C for 1h20m. The NP (approx. 2.7 nm by 3.0 nm) shown in (c) remained at up to 800°C for 20 min; the insert shows the NP's FFT and its characteristic (001) and (002) reflections. Our particles are very close to stoichiometry, resulting in very successful phase transformation from A1 to $L1_0$ [5].

References

[1] A. Delattre, et al., Small, **6**(8), 932 (2010).
[2] J. E. Wittig et al., Microsc. Microanal., **16** (Suppl. 2) (2010).
[3] O. Dmitrieva et al., J. of Crystal Growth, **303**, 645 (2007).
[4] T. Miyazaki et al., Phys. Rev. B, **72**, 144419 (2005).
[5] A portion of this research was conducted at the SHaRE User Facility, which is sponsored by the Division of Scientific User Facilities, Office of Basic Energy Sciences, U.S. Dept. of Energy. Financial support from the Agence Nationale de la Recherche (ANR, projet PNANO Camaieu) is also acknowledged.

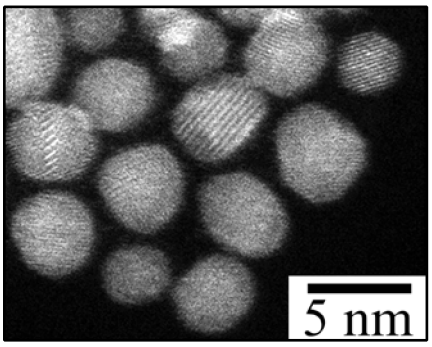
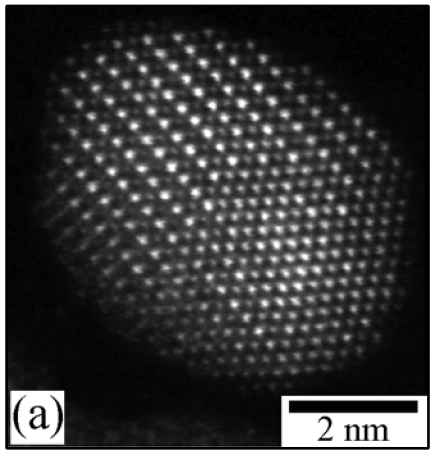


FIG. 1. HAADF-STEM image of ex-situ annealed FePt NPs.



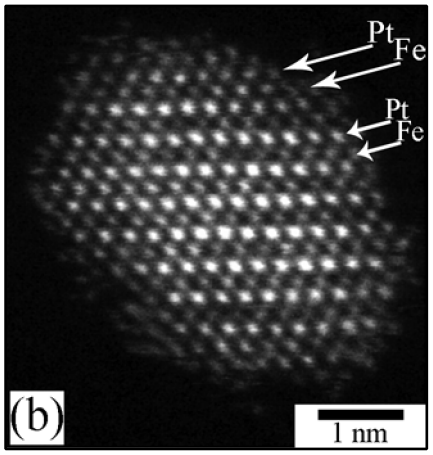


FIG. 2. HAADF-STEM images of a partially ordered NP (a), and a fully ordered NP (b).

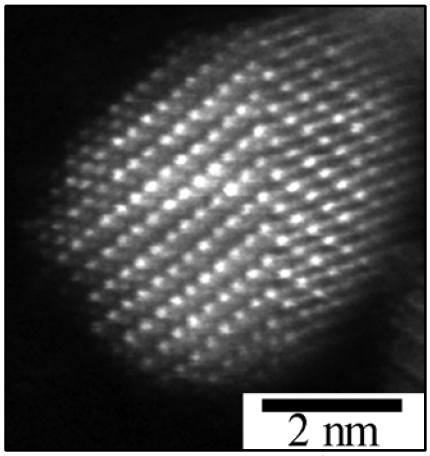
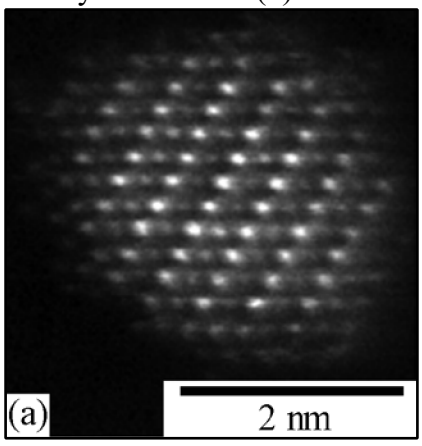
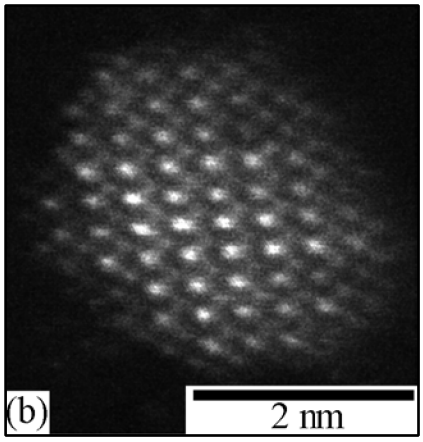


FIG. 3. HAADF-STEM image of a fully ordered twinned NP.





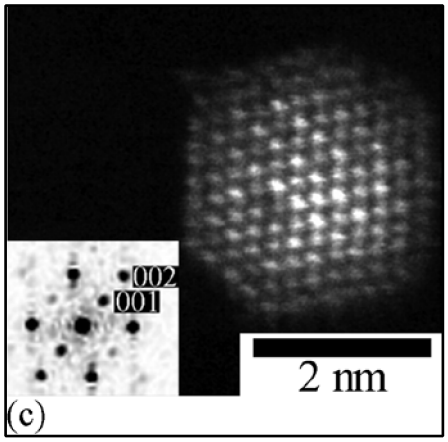


FIG. 4. HAADF-STEM images of three fully ordered NPs; their sizes approach the limit for ordering.

https://doi.org/10.1017/S1431927611003473 Published online by Cambridge University Press