

## Interface structures in FePt/Fe<sub>3</sub>Pt hard-soft exchange-coupled magnetic nanocomposites

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Self-assembly of FePt and Fe<sub>3</sub>O<sub>4</sub> nanoparticles of different sizes led to various FePt–Fe<sub>3</sub>O<sub>4</sub> nanocomposites. Annealing the composite under reducing atmosphere at 650 and 700 °C induced magnetically hard FePt phase and magnetically soft Fe<sub>3</sub>Pt phase. The FePt and Fe<sub>3</sub>Pt phases were either linked by a common interface or coexisted within one grain as domains with sizes < 10 nm. This ensures the effective exchange coupling of magnetically hard and soft phases. High-resolution transmission electron microscopy studies provide detailed structural characterization for the FePt based nanocomposites. © 2003 American Institute of Physics. [DOI: 10.1063/1.1578515]

In comparison to that of soft magnetic materials, the performance of conventional bulk permanent magnetic materials is limited by its relatively low magnetization. It has been proposed that the two-phase materials with exchange-coupled magnetically hard and soft phases may greatly enhance the energy products.<sup>1–3</sup> A critical requirement for exchange coupling is that the dimension of the soft phase should be comparable to the domain wall width of the hard phase, which is typically on the order of 10 nm. This has posed significant challenges in both material processing and characterization. Recently, self-assembly of two-component FePt- and Fe-based nanoparticles has been used as an approach to preparing nanocomposite materials with enhanced energy product.<sup>4</sup> The exchange coupled isotropic FePt–Fe<sub>3</sub>Pt composite has energy product of 20 MG Oe, 50% higher than that expected theoretically from a single phase, nonexchange-coupled, isotropic FePt.

To ensure the effective exchange coupling, studying the nanometer-scale interface between magnetically hard and soft phases is essential. In this study, we use high-resolution transmission electron microscopy (HRTEM) and energy dispersive x-ray spectrometry (EDS) to characterize interface structures between the magnetically hard (FePt) and soft (Fe<sub>3</sub>Pt) phases. We have observed an Fe-rich phase within the nanocomposites and identified the phase to be Fe<sub>3</sub>Pt in sizes of < 10 nm. The Fe<sub>3</sub>Pt nanocrystals are in direct contact with the hard FePt nanocrystals through either common interfaces or coexisting within a single grain.

The as-synthesized samples used for this study were either FePt (4 nm) single-phase self-assembly, or FePt-based nanocomposites obtained from Fe<sub>58</sub>Pt<sub>42</sub>/Fe<sub>3</sub>O<sub>4</sub> binary assembly. The sizes of nanoparticles in the binary assembly were 4 nm for FePt and 4, 8, and 12 nm for Fe<sub>3</sub>O<sub>4</sub>, and the mass ratios (FePt:Fe<sub>3</sub>O<sub>4</sub>) were 10:1 and 5:1. The samples

were annealed under Ar+5% H<sub>2</sub> at 600 or 700 °C for 1 h (for the single-phase self-assembly) and at 650 or 700 °C for 1 h (for binary assembly). Two kinds of TEM samples were prepared: (a) assemblies deposited on TEM grids, and (b) assemblies deposited on NaCl solid substrates. After dissolving the substrate by water, the films were picked up onto TEM grids, followed by ion milling to produce an electron beam transparent area. After annealing in Ar+5% H<sub>2</sub>, the Fe<sub>3</sub>O<sub>4</sub> particles were reduced to Fe, and FePt/Fe-rich nanocomposites were formed. Structural analysis was carried out using a Hitachi HF 2000 field emission TEM operated at 200 kV and a JEOL 4000EX TEM operated at 400 kV.

For the self-assembled FePt and Fe<sub>3</sub>O<sub>4</sub> nanoparticles deposited on TEM grids, annealing induced particle aggregation into larger particles with sizes in range of 10–20 nm (for the 4 nm FePt, 4 nm Fe<sub>3</sub>O<sub>4</sub> sample) and 10–50 nm (for the 4 nm FePt, 8 nm Fe<sub>3</sub>O<sub>4</sub> and 4 nm FePt, 12 nm Fe<sub>3</sub>O<sub>4</sub> samples). The agglomerated particles consist of several smaller nanocrystallites. Electron diffraction indicated that in all of the annealed samples, FePt phase has an ordered *L1*<sub>0</sub> (fct) structure corresponding to a magnetically hard phase; FePt nanoparticles have three-dimensional-randomly oriented *c* axis. A structure—magnetic properties—magnetic reversal mechanism relationship for single phase FePt has been published elsewhere.<sup>5</sup>

Quantitative EDS analyses were carried out with a beam size of ~3 nm for different FePt and Fe<sub>3</sub>O<sub>4</sub> nanocomposite samples. The ratio of *K* factors for EDS quantification was measured from a standard sample of Fe<sub>58</sub>Pt<sub>42</sub>, and the result is  $K_{\text{FePt}} = 2.04 \pm 0.10$  under our experimental conditions. Figure 1 shows EDS spectrum for a typical single phase FePt sample. The inset in Fig. 1 is an EDS spectrum for some small nanocrystallites within big particles, indicating a composition of Fe:Pt=3.18±0.15, a composition of magnetically soft phase Fe<sub>3</sub>Pt. The main EDS results are as follows: (1) Some of the aggregated bigger particles have a composition of FePt, while some other aggregates are Fe-rich. (2)

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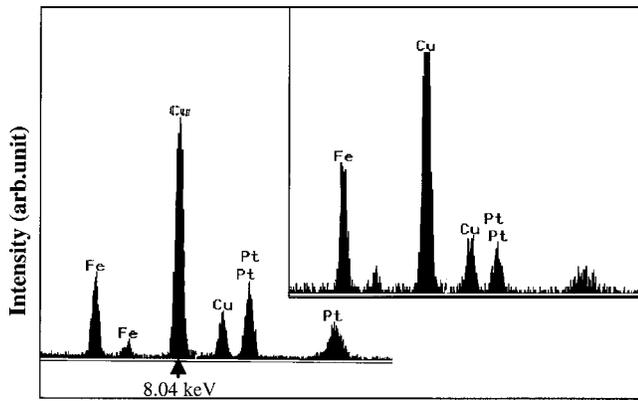


FIG. 1. EDS spectrum for a typical single phase FePt particle. The inset shows a typical spectrum from some smaller nanocrystallites within big particles, confirming an  $\text{Fe}_3\text{Pt}$  composition. (sample: 4 nm FePt and 12 nm  $\text{Fe}_3\text{O}_4$  nanocomposite, annealed at 650 °C).

Some of the small nanocrystallites with sizes  $\leq 10$  nm within the large aggregates have composition of  $\text{Fe}_3\text{Pt}$  phase.

HRTEM were further applied to identify the structurally distinctive FePt and  $\text{Fe}_3\text{Pt}$  phases within the large aggregates, and nanoscale interfaces between them. The  $L1_0$  FePt phase has a chemically ordered fct structure with  $a = 0.3861$  nm and  $c = 0.3788$  nm;  $\text{Fe}_3\text{Pt}$  phase has a structure of either disordered fcc or ordered  $L1_2$  structure with  $a = 0.3730$  nm. Although these three kinds of structures have very close lattice parameters, but  $L1_0$  (fct) FePt and  $L1_2$   $\text{Fe}_3\text{Pt}$  have different ordered Fe and Pt distributions in the unit cells, they will have different  $[001]$  projected potentials with different composition modulation periodicities, while the fcc structured  $\text{Fe}_3\text{Pt}$  does not. Also, the  $L1_0$  (fct) FePt has a layered Fe and Pt distribution for the  $[100]$  or  $[010]$  projection [see Fig. 2 and the insets in Figs. 3(a), 3(b), 5(a), and 5(b)]. For thin samples, HRTEM image can be interpreted as a projected potential image of the sample under certain imaging conditions.<sup>6</sup> Thus, by using HRTEM images of  $\langle 001 \rangle$  oriented particles, we will be able to identify and distinguish different phases. The typical objective lens defo-

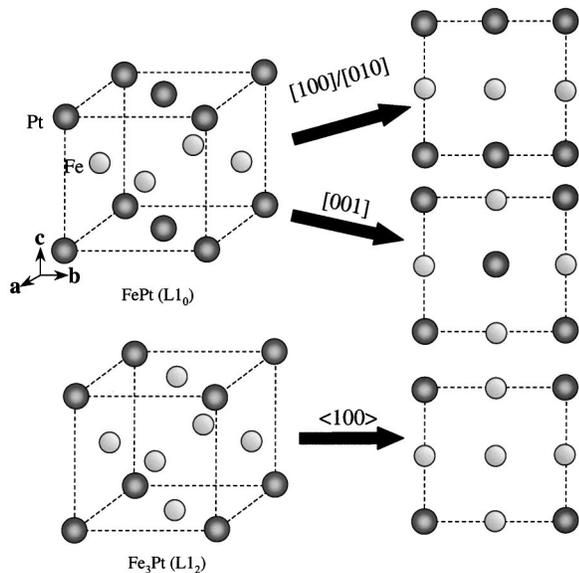


FIG. 2. Structure models of FePt ( $L1_0$ ) and  $\text{Fe}_3\text{Pt}$  ( $L1_2$ ) and the corresponding projections of the structures along different zone axis.

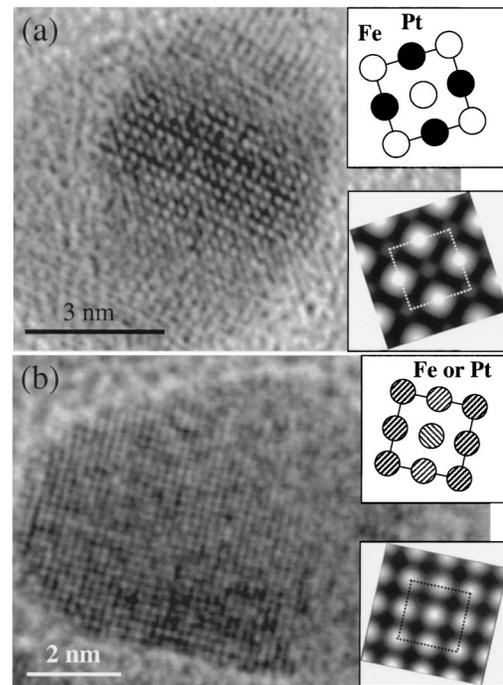


FIG. 3. HRTEM images for different phases in Fe–Pt nanocomposites. (a)  $[001]$   $L1_0$  (fct) FePt particle with the insets showing schematically the  $[001]$   $L1_0$  structure projection and simulated HRTEM image ( $\Delta f = -12$  nm, thickness = 4.56 nm). (b)  $\langle 001 \rangle$  fcc  $\text{Fe}_3\text{Pt}$  particle with insets showing schematic  $\langle 001 \rangle$  fcc projection and simulated HRTEM image ( $\Delta f = 0$  nm, thickness = 5.7 nm).

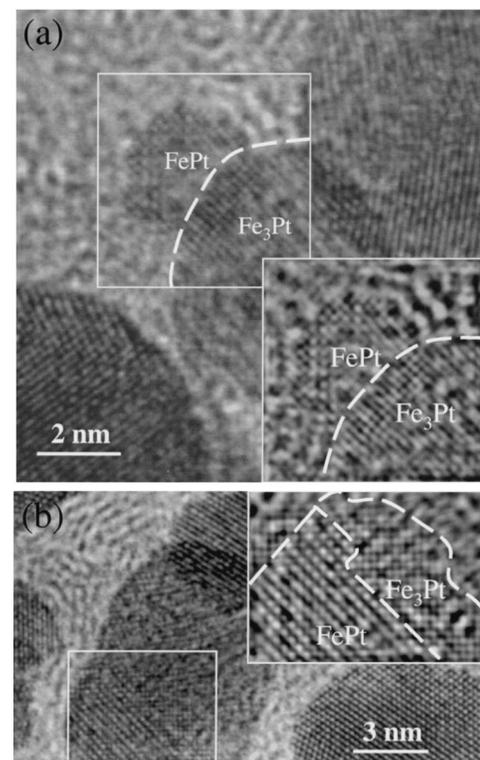


FIG. 4. HRTEM images of an FePt/ $\text{Fe}_3\text{Pt}$  interface in Fe–Pt based nanocomposites deposited on TEM grids. (a) FePt and  $\text{Fe}_3\text{Pt}$  particles are linked by a common interface (sample: 4 nm FePt, 8 nm  $\text{Fe}_3\text{O}_4$ ). (b) FePt and  $\text{Fe}_3\text{Pt}$  phases coexist within a common grain as domains (sample: 4 nm FePt, 8 nm  $\text{Fe}_3\text{O}_4$ ). The insets in (a) and (b) show the Fourier filtered HRTEM images from the correspondent areas as marked by the rectangular in (a) and (b), respectively.

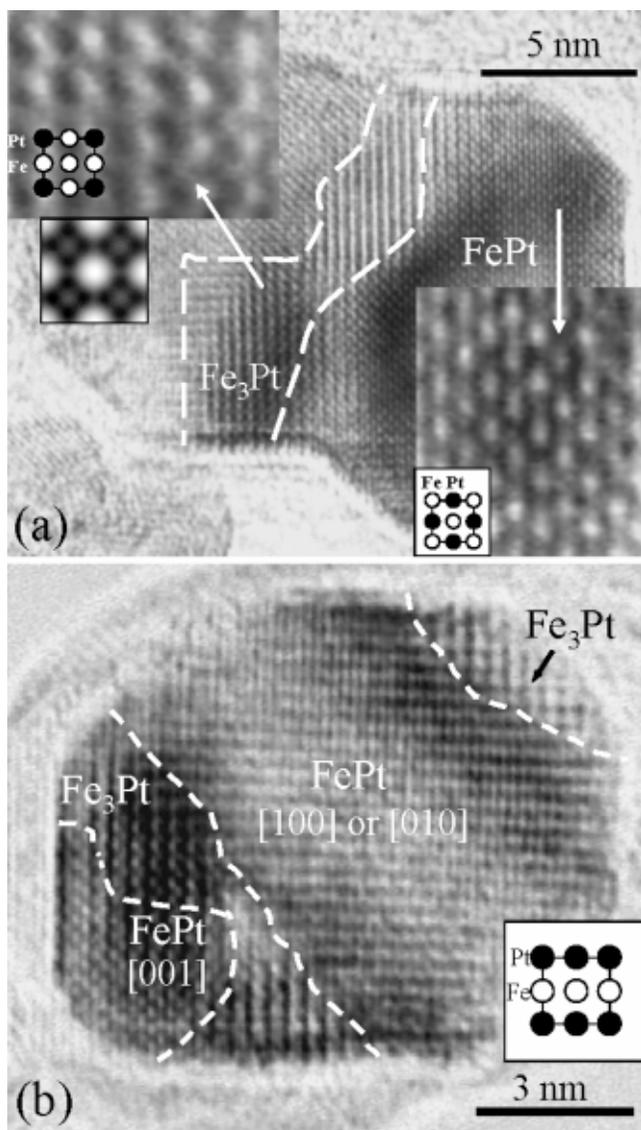


FIG. 5. HRTEM images for the Fe–Pt based nanocomposites deposited onto a solid substrate, showing nanometer-scale FePt/Fe<sub>3</sub>Pt interfaces. The Fe<sub>3</sub>Pt phase has an ordered  $L1_2$  structure (sample: 4 nm FePt, 8 nm Fe<sub>3</sub>O<sub>4</sub>). (a) The insets show the HRTEM images with a higher magnification for the Fe<sub>3</sub>Pt and FePt phases, as well as the schematic  $\langle 001 \rangle$  projection of Fe<sub>3</sub>Pt ( $L1_2$ ) and  $[001]$  projection of FePt ( $L1_0$ ), respectively. The image simulation at  $\Delta f = 30$  nm, thickness = 11.4 nm for Fe<sub>3</sub>Pt ( $L1_2$ ) is also shown in the inset. (b) FePt phase has different orientated  $c$  axis ( $[001]$ ,  $[100]$ , or  $[010]$ ) within a common particle. The inset shows schematically the  $[100]$  or  $[010]$   $L1_0$  structure projection.

cus ( $\Delta f$ ) values we have used are  $-50$  to  $50$  nm; the typical sample thickness is in a range of  $4$ – $12$  nm.

Figure 3(a) shows a typical HRTEM image of a  $[001]$  oriented  $L1_0$  (fct) FePt particle with a strong composition modulation. Figure 3(b) shows a HRTEM image of a  $\langle 100 \rangle$  oriented fcc Fe<sub>3</sub>Pt particle without composition modulation. No HRTEM image for a single  $L1_2$  Fe<sub>3</sub>Pt particle was ob-

served, please see inset in Fig. 5(a) for a typical HRTEM image of  $L1_2$  Fe<sub>3</sub>Pt phase. The insets in Figs. 3(a), 3(b), and 5(a) also show the simulated HRTEM images corresponding to the experimental images. The weak contrast of Fe atoms in the simulated images cannot be observed experimentally due to the limited resolution and the background from the amorphous carbon film.

Figure 4 shows the FePt/Fe<sub>3</sub>Pt interface for the samples deposited onto TEM grids. In Fig. 4(a) the FePt and Fe<sub>3</sub>Pt particles were linked but retain their own particles; In Fig. 4(b) FePt and Fe<sub>3</sub>Pt phases are coexistence as domains within a single grain.

For the samples deposited on solid substrates, the EDS results and particle aggregation morphology are very similar to the results observed from the samples deposited on TEM grids. But HRTEM data reveal that, in the samples deposited on TEM grids, Fe<sub>3</sub>Pt phase has a fcc structure (see Fig. 4), while in the samples deposited on solid substrates Fe<sub>3</sub>Pt phase has an ordered  $L1_2$  structure (see Fig. 5). Figure 5(a) and 5(b) show two examples for  $L1_0$  FePt/ $L1_2$  Fe<sub>3</sub>Pt interfaces. Figure 5(b) indicates that sometimes the FePt phase has a randomly orientated  $c$  axis even within a single coalescent particle.

Mostly, FePt and Fe<sub>3</sub>Pt phases coexist as different domains with sizes  $\leq 10$  nm within a common grain [see Figs. 4(b), 5(a), and 5(b)], displaying an excellent magnetically hard/soft phases nanocomposite. This microstructure is consistent with the measured magnetic properties from these samples.<sup>4</sup> The images also show that FePt and Fe<sub>3</sub>Pt phases have the same orientation as defined by their fcc crystal structure, and the interfaces between FePt and Fe<sub>3</sub>Pt phases are completely coherent without misfit dislocation.

In summary, the nanometer-scale magnetically hard-soft interfaces of FePt/Fe<sub>3</sub>Pt have been identified for the Fe–Pt based nanocomposites. Annealing at  $650$  and  $700$  °C induced soft phase Fe<sub>3</sub>Pt with sizes  $\leq 10$  nm. The FePt and Fe<sub>3</sub>Pt particles were either linked by a common interface or coexisted within a single grain as domains with sizes  $\leq 10$  nm. This analysis provides the structural relations between magnetically hard and soft phases in this exchange coupled FePt based nanocomposites.

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<sup>1</sup>E. F. Kneller and R. Hawig, IEEE Trans. Magn. **27**, 3588 (1991).

<sup>2</sup>R. Skomski and J. M. D. Coey, Phys. Rev. B **48**, 15812 (1993).

<sup>3</sup>T. Schrefl, H. Kronmüller, and J. Fidler, J. Magn. Magn. Mater. **127**, L273 (1993).

<sup>4</sup>H. Zeng, J. Li, J. P. Liu, Z. L. Wang, and S. Sun, Nature (London) **420**, 395 (2002).

<sup>5</sup>H. Zeng, J. Li, Z. L. Wang, J. P. Liu, and S. Sun, IEEE Trans. Magn. **38**, 2598 (2002).

<sup>6</sup>High Resolution Transmission Electron Microscopy—Theory and Applications, edited by P. Buseck, J. M. Cowley, and L. Eyring (Oxford University Press, Oxford, 1989).