

Curie temperatures of annealed FePt nanoparticle systems

Chuan-Bing Rong, Yang Li, and J. Ping Liu^{a)}

Department of Physics, University of Texas at Arlington, Arlington, Texas 76019

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The chemically synthesized $\text{Fe}_x\text{Pt}_{100-x}$ nanoparticles with controlled compositions were annealed to transfer the disordered face-centered-cubic structure to the ordered structure. It was found that the $L1_0$ FePt structure can be formed in the wide compositional region of $x=40$ – 68 , and lower or higher Fe content leads to formation of the $L1_2$ FePt_3 or Fe_3Pt phase, respectively. The Néel temperature of $L1_2$ FePt_3 phase and Curie temperatures (T_C) of $L1_0$ FePt and $L1_2$ Fe_3Pt phases are all strongly composition dependent. The room-temperature saturation magnetization has an abnormal dependence on x which is caused by the low T_C of Fe_3Pt phase with $x=75$ – 79 . The big difference in T_C between the heating and cooling thermomagnetic curves of the Fe–Pt alloys with $x=79$ – 90 can be attributed to the difference of $\alpha \leftrightarrow \gamma$ phase transition temperature during heating and cooling. On the other hand, T_C of the $L1_0$ FePt nanoparticles was found to be strongly size dependent.

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I. INTRODUCTION

The interesting magnetic properties of the bulk $\text{Fe}_x\text{Pt}_{100-x}$ materials have been studied in the whole compositional region. For $x=25$ antiferromagnetic order was found,^{1,2} around $x=50$ the alloy shows very large magnetic anisotropy owing to the formation of chemically ordered face-centered-tetragonal (fct) structure.^{3,4} Near $x=75$ large volume instability (Invar effect) is observed in the $L1_2$ Fe_3Pt phase (γ_1).^{5,6} The most recent interests in FePt nanostructured materials have been focused on the ferromagnetic $L1_0$ FePt phase (γ_2) because of their potential applications in ultrahigh-density magnetic recording^{7,8} and advanced permanent magnets^{9,10} due to its very high uniaxial magnetocrystalline anisotropy and high Curie temperatures. Recently, it was reported that Curie temperature (T_C) of sputtered FePt films is composition dependent in the range of 47.5–54.4 at. % Fe.^{11–13} More interestingly, reduction of T_C with decreasing dimension of the materials has also been observed in $L1_0$ FePt nanoparticles¹⁴ and other ferromagnets.^{15,16} In order to understand magnetic ordering of the nanostructured ferromagnetic phases in a wide compositional range, the annealed FePt nanocrystalline films deposited by nanoparticles have been studied with a composition range of 15–90 at. % Fe. The size dependence of T_C of $L1_0$ FePt nanoparticles has also been studied.

II. EXPERIMENTS

The disordered face-centered-cubic (fcc) $\text{Fe}_x\text{Pt}_{100-x}$ nanoparticles were chemically synthesized by the standard airless chemical solution procedures.^{7,17} The composition was controlled by adjusting the molar ratio of iron pentacarbonyl $\text{Fe}(\text{CO})_5$ to platinum acetylacetonate $\text{Pt}(\text{acac})_2$. The synthesized nanoparticles were then deposited on a Si substrate and annealed under forming gas ($\text{Ar}+7\% \text{H}_2$) at 973 K

for 1 h to transfer the disordered fcc structure to the ordered $L1_0$ or $L1_2$ structure. The composition of the synthesized FePt nanoparticles was checked by energy dispersive x-ray (EDX) analysis. The crystalline structure was determined by x-ray diffraction (XRD). The room-temperature magnetic properties were studied by a superconducting quantum interference device (SQUID) magnetometer with a maximum applied field of 7 T. Thermomagnetic curves were measured by a physical property measurement system (PPMS) with high-temperature vibrating sample magnetometer.

III. RESULTS AND DISCUSSIONS

Figure 1 gives the composition dependence of the 4 nm synthesized $\text{Fe}_x\text{Pt}_{100-x}$ nanoparticles on the molar ratio of $\text{Fe}(\text{CO})_5$ to $\text{Pt}(\text{acac})_2$. The error bar is based on the statistical standard deviation of the EDX analysis. It shows that the composition $x=15$ – 90 can be obtained by adjusting the molar ratio of precursors. This result is similar to that of Ref. 17.

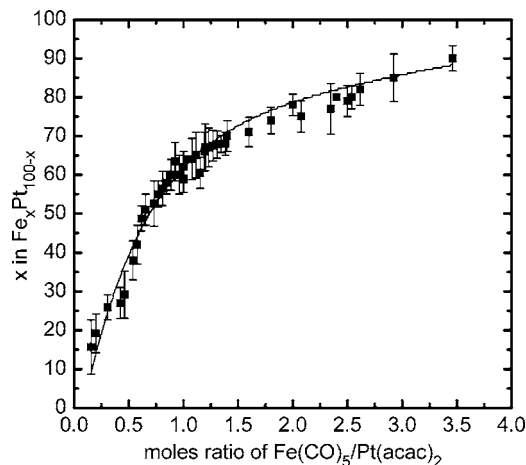


FIG. 1. The dependence of x on the molar ratio of $\text{Fe}(\text{CO})_5$ to $\text{Pt}(\text{acac})_2$.

^{a)}Electronic mail: pliu@uta.edu

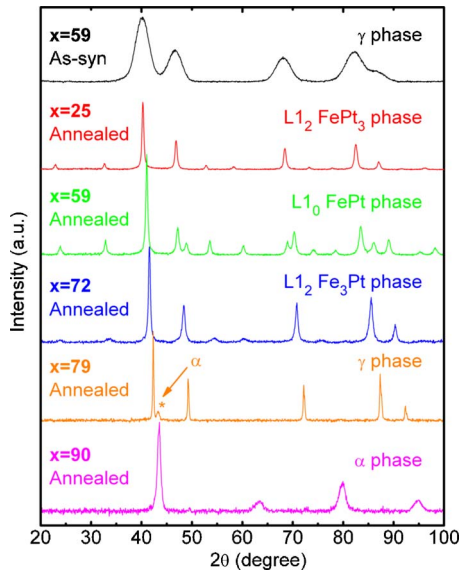


FIG. 2. (Color online) XRD patterns of the as-synthesized nanoparticles with $x=59$ and the annealed films with different compositions, i.e., $x=25$, 59, 72, 79, and 90.

XRD patterns of Fe_xPt_{100-x} films were recorded after being annealed at 973 K in forming gas for 1 h. Figure 2 shows the XRD patterns of the annealed films with five different compositions $x=25$, 59, 72, 79, and 90. A typical XRD pattern for the as-synthesized nanoparticles is also shown in the figure for comparison. It should be noted that XRD spectra of all the as-synthesized samples showed a disordered γ phase in the whole compositional region. When the assembled films were annealed at 973 K, on the other hand, Fe₂₅Pt₇₅ exhibits a Cu₃Au-type γ_3 -FePt₃ phase with L₁₂ structure. It was found that for the annealed Fe₅₉Pt₄₁ film the superlattice reflections (001) and (110) appear in the XRD spectra, indicating the formation of an ordered L₁₀ γ_2 -FePt phase. For Fe₇₂Pt₂₈, the annealing resulted in the formation of L₁₂ γ_1 -Fe₃Pt phase. With increasing Fe content to $x=79$, XRD pattern revealed that the main phase was γ -FePt phase with fcc structure, while a small amount of α -(Fe,Pt) was also found. Further increase of Fe content led to a decrease of γ -FePt phase content and an increase of α -FePt phase content. When $x=90$, the annealed films consisted of only α -FePt phase, as shown in Fig. 1. In general, the peak broadening of the annealed Fe_xPt_{100-x} films became less pronounced compared to the as-synthesized nanoparticles since the grains became coarse upon annealing. The average grain size was 4 nm for the as-synthesized nanoparticles, while it was around 10–20 nm after annealing on Si substrates, determined by the analysis of XRD patterns using Scherrer formula.

Figure 3 shows the dependence of Néel temperature T_N or Curie temperature T_C on composition of the annealed nanoparticles. The magnetic phase transition temperatures were determined by the intersection of extrapolations of the greatest slope and flat region in the M - T curves. It was reported that FePt₃ is antiferromagnetic in the chemically ordered state.^{1,2} The XRD patterns show that the ordered phase FePt₃ with Cu₃Au cubic L₁₂ structure can be obtained when $x \leq 40$, which is similar to the condition shown in the phase

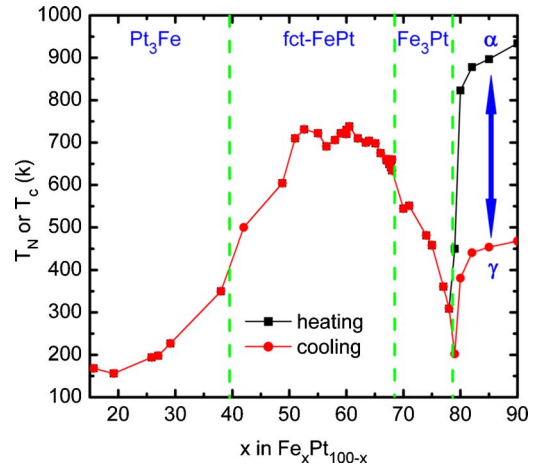


FIG. 3. (Color online) The dependence of T_N or T_C on x of the annealed nanoparticles.

diagram.¹⁸ It was found that T_N of the FePt₃ phase increased with increasing Fe content. An ordered fct FePt ferromagnetic phase with L₁₀ structure formed within the compositional region $x=40$ –69. T_C of the fct phase increased fast when $x \leq 50$ and reached the maximum about 730 K when $x=51$ –64 and then dropped with increasing x . For $69 \leq x \leq 78$, Fe₃Pt phase with L₁₂ structure was formed after annealing. It can be seen that T_C decreased dramatically from 550 K with $x=70$ to 310 K with $x=79$. More interestingly, it was found that there is a big difference between the heating and cooling thermomagnetic curves of the Fe–Pt alloys with Fe content of 80–90 at. %. Figure 4 shows the typically heating and cooling M - T curves of the Fe₈₀Pt₂₀ sample. This phenomenon can be attributed to the difference of $\alpha \leftrightarrow \gamma$ phase transition temperature during heating and cooling.¹⁹ One can see from the Fe–Pt phase diagram¹⁸ that the phase transitional temperature from α to γ phase on heating is far higher than that of γ to α on cooling.

Figure 5 gives the dependence of saturation magnetization M_s and coercivity H_c on the composition of annealed nanoparticles. M_s at room temperature, which was measured under 7 T, increases monotonously almost in the whole compositional region except in the region $75 < x \leq 79$ where M_s of the Fe₃Pt phase drops. This is caused by the low Curie

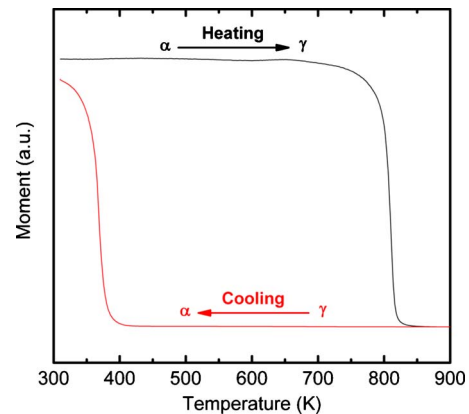


FIG. 4. (Color online) The typically heating and cooling M - T curves of the Fe₈₀Pt₂₀ sample.

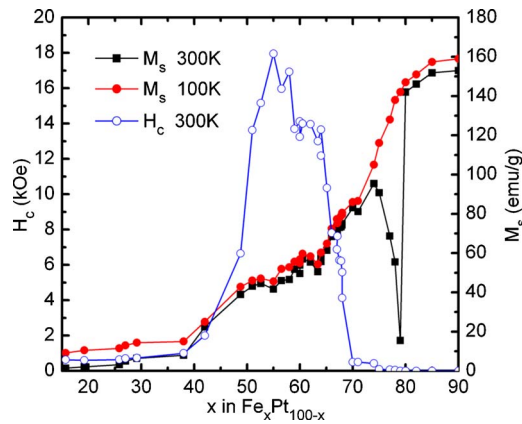


FIG. 5. (Color online) The dependence of M_s and H_c on x of annealed nanoparticles.

temperature (near or lower than room temperature) of Fe_3Pt phase in this special compositional region since there is no dip in the M_s - x curve at 100 K, as shown in Fig. 5. H_c is also very sensitive to composition. Nonzero coercivity can be obtained only in the region $x=42$ – 68 where $L1_0$ phase was formed. The maximum H_c is 18 kOe at $x=55$. With both high M_s and H_c , the maximum energy product $(BH)_{\max}$ about 17 MG Oe can be obtained at $x=66$ where $H_c=7.6$ kOe.

Beside the composition dependence, it was also found that T_C decreases fast with decreasing dimensions of the materials. Our recently developed salt-matrix annealing method²⁰ allows us to tune the size of the monodisperse $L1_0$ FePt particles and to obtain a direct correlation between particle size and Curie temperature. Figure 6 shows M - T curves of the 3 and 15 nm $L1_0$ FePt nanoparticles which are obtained by the salt-matrix. It shows that T_C of the 3 nm particles is substantially lower than that of 15 nm particles. A systematic study of the size dependence of T_C has been reported elsewhere.¹⁴ The size dependent behavior, as discussed in Refs. 14–16, can be explained by the finite-size-scaling theory.^{21,22}

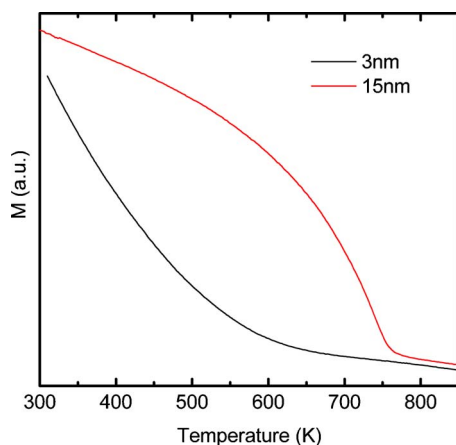


FIG. 6. (Color online) M - T curves of the 3 and 15 nm $L1_0$ nanoparticles which are obtained by the salt-matrix method.

IV. CONCLUSION

The FePt nanoparticles with controlled composition have been prepared by chemical synthesis. The ordered phases with different structures were obtained by annealing the particles at 973 K for 1 h. It is found that the $L1_0$ FePt structure can be formed in a wide compositional region of $x=40$ – 68 , while the FePt_3 or Fe_3Pt with $L1_2$ structure are formed with lower or higher Fe contents. The Curie temperatures of the $L1_0$ FePt phase are strongly composition dependent and are higher than that of Fe_3Pt phase. The abnormal dependence of M_s at room temperature on x is caused by the low T_C of Fe_3Pt phase with $x=75$ – 79 . It was also found that there is a big difference in T_C when measured through the heating and cooling thermomagnetic curves of the Fe–Pt alloys with $x=78$ – 90 . This phenomenon can be attributed to the difference of $\alpha \rightleftharpoons \gamma$ phase transition temperature during heating and cooling. On the other hand, T_C of the $L1_0$ FePt nanoparticles is strongly size dependent.

ACKNOWLEDGMENTS

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