Curie temperatures of annealed FePt nanoparticle systems

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The chemically synthesized FePt<sub>100−x</sub> nanoparticles with controlled compositions were annealed to transfer the disordered face-centered-cubic structure to the ordered structure. It was found that the L1<sub>0</sub> FePt phase can be formed in the wide compositional region of x=40–68, and lower or higher Fe content leads to formation of the L1<sub>2</sub> FePt<sub>x</sub> or Fe<sub>x</sub>Pt phase, respectively. The Néel temperature of L1<sub>2</sub> FePt<sub>x</sub> phase and Curie temperatures (T<sub>C</sub>) of L1<sub>0</sub> FePt and L1<sub>2</sub> Fe<sub>x</sub>Pt phases are all strongly composition dependent. The room-temperature saturation magnetization has an abnormal dependence on x which is caused by the low T<sub>C</sub> of Fe<sub>x</sub>Pt phase with x=75–79. The big difference in T<sub>C</sub> between the heating and cooling thermomagnetic curves of the Fe–Pt alloys with x=79–90 can be attributed to the difference of α⇔γ phase transition temperature during heating and cooling. On the other hand, T<sub>C</sub> of the L1<sub>0</sub> FePt nanoparticles was found to be strongly size dependent.


I. INTRODUCTION

The interesting magnetic properties of the bulk Fe<sub>x</sub>Pt<sub>100−x</sub> materials have been studied in the whole compositional region. For x=25 antiferromagnetic order was found;<sup>1,2</sup> around x=50 the alloy shows very large magnetic anisotropy owing to the formation of chemically ordered face-centered-tetragonal (fcct) structure.<sup>3,4</sup> Near x=75 large volume instability (Invar effect) is observed in the L1<sub>2</sub> Fe<sub>x</sub>Pt phase (γ<sub>1</sub>).<sup>5,6</sup> The most recent interests in FePt nanostructured materials have been focused on the ferromagnetic L1<sub>0</sub> FePt phase (γ<sub>2</sub>) because of their potential applications in ultrahigh-density magnetic recording,<sup>7,8</sup> and advanced permanent magnets<sup>9,10</sup> due to its very high uniaxial magnetocrystalline anisotropy and high Curie temperatures. Recently, it was reported that Curie temperature (T<sub>C</sub>) of sputtered FePt films is composition dependent in the range of 47.5–54.4 at. % Fe.<sup>11–13</sup> More interestingly, reduction of T<sub>C</sub> with decreasing dimension of the materials has also been observed in L1<sub>0</sub> FePt nanoparticles<sup>14</sup> and other ferromagnets.<sup>15,16</sup> 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<sub>C</sub> of L1<sub>0</sub> FePt nanoparticles has also been studied.

II. EXPERIMENTS

The disordered face-centered-cubic (fcc) Fe<sub>x</sub>Pt<sub>100−x</sub> nanoparticles were chemically synthesized by the standard airless chemical solution procedures.<sup>7,17</sup> The composition was controlled by adjusting the molar ratio of iron pentacarbonyl Fe(CO)<sub>5</sub> to platinum acetylacetone Pt(acac)<sub>2</sub>. The synthesized nanoparticles were then deposited on a Si substrate and annealed under forming gas (Ar+7%H<sub>2</sub>) at 973 K for 1 h to transfer the disordered fcc structure to the ordered L1<sub>0</sub> or L1<sub>2</sub> 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 FePt<sub>100−x</sub> nanoparticles on the molar ratio of Fe(CO)<sub>5</sub> to Pt(acac)<sub>2</sub>. 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 Fe(CO)<sub>5</sub> to Pt(acac)<sub>2</sub>.](Image:340x78 to 532x249)
XRD patterns of Fe$_{x}$Pt$_{100-x}$ 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 $\gamma$ phase in the whole compositional region. When the as-synthesized films were annealed at 973 K, on the other hand, Fe$_{25}$Pt$_{75}$ exhibits a Cu$_3$Au-type $\gamma_2$-FePt$_3$ phase with $L1_2$ structure. It was found that for the annealed Fe$_{50}$Pt$_{41}$ film the superlattice reflections (001) and (110) appear in the XRD spectra, indicating the formation of an ordered $L1_2$ $\gamma_2$-FePt phase. For Fe$_{75}$Pt$_{25}$, the annealing resulted in the formation of $L1_2$ $\gamma_2$-FePt$_3$ phase. With increasing Fe content to $x=79$, XRD pattern revealed that the main phase was $\gamma$-FePt phase with fcc structure, while a small amount of $\alpha$-(Fe,Pt) was also found. Further increase of Fe content led to a decrease of $\gamma$-FePt phase content and an increase of $\alpha$-FePt phase content. When $x=90$, the annealed films consisted of only $\alpha$-FePt phase, as shown in Fig. 1. In general, the peak broadening of the annealed Fe$_{x}$Pt$_{100-x}$ 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 Neél 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 FePt$_3$ is antiferromagnetic in the chemically ordered state. The XRD patterns show that the ordered phase FePt$_3$ with Cu$_3$Au cubic $L1_2$ structure can be obtained when $x \leq 40$, which is similar to the condition shown in the phase diagram. It was found that $T_N$ of the FePt$_3$ phase increased with increasing Fe content. An ordered $fct$ FePt ferromagnetic phase with $L1_0$ 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 $69 \leq x \leq 78$, Fe$_x$Pt phase with $L1_2$ 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 typical heating and cooling $M$-$T$ curves of the Fe$_{80}$Pt$_{20}$ sample. This phenomenon can be attributed to the difference of $\alpha \leftrightarrow \gamma$ phase transition temperature during heating and cooling. One can see from the Fe–Pt phase diagram that the phase transitional temperature from $\alpha$ to $\gamma$ phase on heating is far higher than that of $\gamma$ to $\alpha$ 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 $\leq x \leq 79$ where $M_s$ of the Fe$_x$Pt phase drops. This is caused by the low Curie
temperature (near or lower than room temperature) of Fe3Pt phase in this special compositional region since there is no dip in the $M_r-x$ curve at 100 K, as shown in Fig. 5. $H_c$ is also very sensitive to composition. Nonzero coercivity can be obtained elsewhere.\textsuperscript{14} The size dependent behavior, as discussed in Refs. 14–16, can be explained by the finite-size-scaling theory.\textsuperscript{21,22}

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 method\textsuperscript{20} allows us to tune the size of the monodisperse $L1_0$ FePt nanoparticles 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 nanoparticles is substantially lower than that of 15 nm particles. A systematic study of the size dependence of $T_C$ has been reported elsewhere.\textsuperscript{14} The size dependent behavior, as discussed in Refs. 14–16, can be explained by the finite-size-scaling theory.\textsuperscript{21,22}

\section*{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$_3$Pt 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 Fe3Pt phase. The abnormal dependence of $M_s$ at room temperature on $x$ is caused by the low $T_C$ of Fe3Pt 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 $\alpha\Leftrightarrow\gamma$ phase transition temperature during heating and cooling. On the other hand, $T_C$ of the $L1_0$ FePt particles is strongly size dependent.

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