Observation of two kinds of ESR spectra in FePt nanoparticles

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Abstract. The size effects on magnetic properties of FePt nanoparticles were investigated through ESR experiment in X-band at room temperature. For particle size ($D$) of $> 2.6$ nm, the absorption spectra were the Gaussian type, whereas for $D = 2.0$ nm, it was reproduced with the summation of the Gaussian and Lorentzian types. It has been well known that a face-centered-tetragonal (fct) structure becomes unstable for $D \leq 2$-4 nm. Two kinds of magnetic components for FePt nanoparticles with $D = 2.0$ nm, observed in the ESR spectrum at room temperature, are considered to be attributed to the coexistence of the particles with fct structure and those with face-centered cubic structures.

1. Introduction

Magnetic nanoparticles prefer a single domain structure to multi domain structure, due to the decrease of the magnetostatic energy relative to the magnetic domain wall energy. This single domain structure has an advantage on constructing magnetic recording media of high bit. When the magnetic nanoparticles have a large coercivity ($H_C$), the application for memory devices is promising. The FePt nanoparticle with large magnetocrystalline anisotropy has attracted much attention as a candidate material for memory devices.

FePt originally has two stable structures such as face-centered-cubic (fcc) and face-centered-tetragonal (fct). In the fcc structure, the alignment of Fe and Pt atoms in crystalline is random, while in the fct structure, Fe and Pt atoms are regularly arranged in the layer manner. The fcc structure magnetically exhibits a disorder phase. By contrast, the fct structure with magnetic order has a large magnetocrystalline anisotropy ($= 6.6 \times 10^7$ erg/cm$^3$) and a high $H_C$ ($= 7850$ Oe) [1]. In that sense, the fct structure is desirable for magnetic recording media. However, there have been theoretical and experimental reports revealing that the fct structure in the FePt nanoparticle becomes unstable at the particle size ($D$) of $< 2$-4 nm [2, 3]. According to the theoretical simulation, the formation of the fct structure has been quite difficult for $D < 2$ nm. Iwamoto et al. reported that $H_C$ of the FePt nanoparticles decreased with decreasing $D$ at high temperature ($T$) (i.e. 300 K), whereas for $D \geq 3.7$
nm $H_C$ increased with decreasing $D$ at $T = 10$ K or low temperature [4]. It is an open question whether the variation of $H_C$ with functions of $T$ and $D$ is related to any structural transition or not.

We investigated physical properties of the FePt nanoparticle with small $D$’s ($\leq 6.0$ nm) at room temperature through ESR experiment in X-band, in addition to X-ray diffraction (XRD) experiment. The ESR spectrum yielded an important information for verifying whether fcc and fct coexist or not.

2. Experiment

FePt nanoparticles were prepared by the procedure described elsewhere [4]. It is usually necessary to anneal the material at high temperatures in order to transform the fcc structure into the fct structure. The present samples were, however, synthesized at low temperatures such as 500-600 K [4]. To avoid the aggregation of nanoparticles, the FePt nanoparticles were coated by a polymer protective agent, poly(N-vinyl-2-pyrrolidone) (PVP). The blocking temperature ($T_B$) and $H_C$ for $D = 2.0, 2.6, 3.4, 3.9$ and $6.0$ nm are summarized in Table 1. The Curie temperature ($T_C$) of the bulk FePt is 750 K, and even in nano size, its value remains at around 700 K [5]. The particle size was estimated from transmission electron microscopy (TEM) study and XRD experiment. The ESR measurements were performed using an X-band spectrometer (JES-RE2X, JEOL Ltd.) at about 9.4 GHz at room temperature. Synchrotron radiation powder XRD measurements at room temperature were carried out at the Photon Factory (PF) of the Institute of Materials Structure Science, the High Energy Accelerator Research Organization (KEK) [6]. The incident X-ray wavelength was 0.68872(5) Å for $D = 2.0$ and 6.0 nm, and 0.68983(1) Å for $D = 2.6, 3.4$ and 3.9 nm, respectively.

Table 1. $T_B$ at $f= 1$Hz and $H_C$ at $T = 300$ K of FePt nanoparticles, used in the present experiment.

| $D$ [nm] | $T_B$ [K] ($f= 1$ Hz) | $H_C$ [Oe] ($T = 300$ K) |
|----------|----------------------|--------------------------|
| 2.0      | 42.9                 | 58 ± 10                  |
| 2.6      | 176                  | 80 ± 10                  |
| 3.4      | > 400 K              | 145 ± 8                  |
| 3.9      | > 400 K              | 108 ± 5                  |
| 6.0      | > 400 K              | 453 ± 5                  |

3. Results and Discussion

Figure 1 shows the XRD patterns of FePt nanoparticles at room temperature for each $D$. The red pattern is the simulation result, based on the bulk FePt with the fct structure. In case of the FePt nanoparticles with $D = 6.0$ nm, the superlattice peaks of (001) and (110) planes peculiar to the fct structure were observed at $2\theta = 10.4^\circ$ and $14.8^\circ$ in the XRD pattern, respectively, though the height of

![Figure 1. XRD patterns of FePt nanoparticles for $D = 2.0, 2.6, 3.4, 3.9$ and $6.0$ nm at room temperature. The red pattern is the simulation result, based on the bulk FePt with fct structure. The superlattice peaks with the plain index of (001) and (110) planes for the fct structure appear at around $2\theta = 10^\circ$ and $15^\circ$, respectively.](image-url)
the superlattice peaks are smaller than that in the typical fct phase. However, the result of the ESR spectrum explained later suggests that the nanoparticles with $D = 6.0$ nm consist of the single magnetic component. Therefore we consider that this XRD pattern indicates that at $D = 6.0$ nm, the fct structure is stably formed. On the other hand, at the smallest $D (= 2.0$ nm), there was no prominent diffraction peak at around $2\theta = 15^\circ$, suggesting that the fct structure is not formed dominantly.

Figure 2 shows the ESR spectrum at room temperature for $D = 2.0$ nm: (a) derivative absorption spectrum and (b) its integral spectrum (open circle). The main resonance was observed at around 330 mT. At a glance, this sharp peak suggests the isotropic nature. However, the integral spectrum exhibits unique symmetry, and it is neither Gaussian nor Lorentzian. Rather the combination of Gaussian and Lorentzian yields a successful result. The values of resonance field ($H_r$) and full-width at half maximum ($\Delta H_{1/2}$) in each line shape are presented in Table 2, together with the data for $D = 2.6, 3.4, 3.9$ and $6.0$ nm. The $\Delta H_{1/2}$ reflects the relaxation time of spin. The Gaussian absorption line reflects the constant spin correlation against time, while the Lorentzian absorption line reflects the rapid decay of the spin correlation function [8]. The ratios of Gaussian and Lorentzian, estimated from the area of integral spectrum, are 59% and 41%, respectively. This indicates that two kinds of magnetic contribution prominently exists at $D = 2.0$ nm. Recalling that the fct structure becomes unstable for $D$ of below 2-4 nm [2, 3], the two contributions are considered to be attributed to the fct structure and fcc structure. The value of $D$ determined by XRD was consistent with that by TEM. We do not think that

![Figure 2](image-url)

**Figure 2.** (a) Derivative absorption spectrum and (b) integral spectrum for FePt nanoparticle with $D = 2.0$ nm at room temperature. The inset of (a) indicates the existence of the sub anomaly at about 170 mT.

![Figure 3](image-url)

**Figure 3.** Derivate absorption spectra and integral spectra for FePt nanoparticles with $D = (a) 2.6, (b) 3.4, (c) 3.9$ and (d) 6.0 nm at room temperature. The red curve represents the fitting curve by the Gaussian function. The detailed fitting parameters, $H_r$ and $\Delta H_{1/2}$, are shown in Table 2.
the FePt nanoparticle has the core-shell structure. Thus, we suppose that nanoparticles with the fct structure and those with the fcc structure coexist in a sample. The fct structure has $T_c$ of near 700 K even at nanometer size [5], while fcc has exhibits no magnetic order. Normally, it is considered that Gaussian component corresponds to the particle with the fct structure, while Lorentzian one does to the particle with the fcc structure. In addition, we noticed the sub anomaly in the ESR spectrum at about 170 mT, which corresponds to nearly a half of main resonant fields, as shown in the inset of Fig. 2(a). Similar phenomenon has already been observed in $\gamma$-Fe$_2$O$_3$, and it was explained by the influence of interparticle interaction [7]. The present nanoparticles were coated with PVP, whereas actually the interparticle magnetic dipolar interaction was not in ignorable level.

Figure 3 shows both the derivative absorption spectra and its integral spectra for nanoparticles with $D \geq 2.6$ nm. With increasing $D$, $H_r$ decreases, suggesting the variation of the effective anisotropy. For nanoparticles with $D \geq 2.6$ nm, the integral spectra are reproduced with the Gaussian type of line shape. It is a convincing result by considering $T_c$ of much higher than room temperature and the stabilization of the fct structure for $D > 2.6$ nm (as shown in Fig. 1). The value of $\Delta H_{1/2}$ tends to increase with increasing $D$ as shown in Table 2. For nanoparticles with $D \geq 2.6$ nm, the sub anomaly at field of about a half of $H_r$ for the main absorption was not observed, probably due to the broadening of of integral spectra.

| $D$ [nm] | Line shape | $H_r$ [mT] | $\Delta H_{1/2}$ [mT] |
|----------|------------|------------|----------------------|
| 2.6      | Gaussian   | 334.0      | 324.4                |
| 3.4      | Gaussian   | 257.1      | 481.0                |
| 3.9      | Gaussian   | 269.2      | 523.6                |
| 6.0      | Gaussian   | 227.1      | 424.3                |

4. Conclusion

The ESR spectra of the FePt nanoparticles with $D = 2.0$, 2.6, 3.4, 3.9 and 6.0 nm were observed at room temperature. The experimental results for the nanoparticles with $D \geq 2.6$ nm indicated that the nanoparticles were composed of magnetically one component, whereas for that with $D = 2.0$ nm two components existed. The fct structure inducing large coercivity has been known to become unstable for $D < 2-4$ nm. The existence of magnetically two components for the nanoparticles with $D = 2.0$ nm suggest that the fct- and fcc-structured particles coexist in the sample.

References

[1] Weller D, Moser A, Folks L, Best M E, Wen Lee, Toney M F, Schwickert M, Thiele J -U and Doerner M F 2000 IEEE. Trans. Magn. 36 10
[2] Takahashi Y K, Koyama T, Ohnuma M, Ohkubo T and Hono K 2004 J. Appl. Phys. 95 2690
[3] Miyazaki T, Kitakami O, Okamoto S, Shimada Y, Akase Z, Murakami Y, Shindo D, Takahashi Y and Hono K 2005 Phys. Rev. B 72 144419
[4] Iwamoto T, Kitamoto Y and Toshima N 2009 Physica B 404 2080
[5] Christdoulide J A, Bonder M J, Huang Y, Zhang Y, Stoyanov S, Hadjioanayis G C, Simopoulos A and Weller D 2003 Phys. Rev. B 68 054428
[6] Fujiwara A, Ishii K, Watanuki T, Suematsu H, Nakao H, Ohwada K, Fujii Y, Murakami Y, Mori T, Kawada H, Kikegara T, Shimomura O, Matsubara T, Hanabusa H, Daisho S, Kitamura S and Katayama C 2000 J. Appl. Crystallogr. 33 1241
[7] Noginova N, Weaver T, Giannelis E P, Bourlinos A B, Atsarkin V A and Demidov V V 2008 Phys. Rev. B 77 014403
[8] Tajiri T, Deguchi H, Kohiki S, Mito M, Takagi S, Mitome M, Murakami Y and Kohno A 2008 J. Phys. Soc. Jpn. 77 074715