Orbital magnetic moment and coercivity of SiO$_2$-coated FePt nanoparticles studied by x-ray magnetic circular dichroism

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We have investigated the spin and orbital magnetic moments of Fe in FePt nanoparticles in the $L_{10}$-ordered phase coated with SiO$_2$ by x-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD) measurements at the Fe $L_{2,3}$ absorption edges. Using XMCD sum rules, we evaluated the ratio of the orbital magnetic moment ($M_{orb}$) to the spin magnetic moment ($M_{spin}$) of Fe to be $M_{orb}/M_{spin} = 0.08$. This $M_{orb}/M_{spin}$ value is comparable to the value (0.09) obtained for FePt nanoparticles prepared by gas phase condensation, and is larger than the values (~0.05) obtained for FePt thin films, indicating a high degree of $L_{10}$ order. The hysteretic behavior of the FePt component of the magnetization was measured by XMCD. The magnetic coercivity ($H_c$) was found to be as large as 1.8 T at room temperature, ~3 times larger than the thin film value and ~50 times larger than that of the gas phase condensed nanoparticles. The hysteresis curve is well explained by the Stoner-Wohlfarth model for non-interacting single-domain nanoparticles with the $H_c$ distributed from 1 T to 5 T.

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The $L_{10}$-ordered alloy FePt has attracted great attention as a material to be used in high-density storage memory devices because FePt possesses a high magnetocrystalline anisotropy in bulk FePt and thin films. In order to increase the storage density of memory devices, FePt nanoparticles are promising materials. FePt nanoparticles prepared by the gas phase preparation method~ and the wet chemical preparation method~ have the fcc structure, in which magnetocrystalline anisotropy disappears. By annealing the nanoparticles at high temperatures, one can transform the structure from the fcc to $L_{10}$, but then the nanoparticles are easily oxidized and are covered by surface oxides. The plasma treatments of FePt nanoparticles followed by in situ flight annealing have been performed to remove the oxidized surfaces~; however, it has simultaneously reduced the magnetic coercivity ($H_c$) as small as 0.038 T~. In addition, high temperature annealing is difficult to implement in existing manufacturing process because it may lead to the coalescence of nanoparticles into larger particles~. Recently, in order to overcome such difficulties, FePt nanoparticles coated with SiO$_2$ were prepared and dispersed before annealing to achieve a high degree of $L_{10}$ order~. FePt nanoparticles prepared by this method have a $H_c$ as large as 1.85 T at 300 K~; of the same order as the value of 3.0 T observed for $L_{10}$-FePt (001) particulate films~, and much larger than the bulk value of 0.16 T~; the thin film value of 0.55 T~; and the value of 0.75 T for microfabricated FePt (001) dots~.

In order to understand the origin of the large $H_c$ and to further improve the properties of the SiO$_2$-coated FePt nanoparticles, microscopic information about the magnetism such as the orbital magnetic moment is important. The chemical state of Fe can be easily distinguished by soft x-ray absorption spectroscopy (XAS), and the orbital and spin magnetic moments of transition-metal 3$d$ orbitals can be measured by soft x-ray magnetic circular dichroism (XMCD) measurements of the 2$p$ core level of the transition element~. Furthermore, in XMCD measurements, one can eliminate extrinsic magnetic signals such as those from oxidized Fe and those from the diamagnetic SiO$_2$ coating. In the present work, we have applied the XAS and XMCD techniques to the SiO$_2$-coated FePt nanoparticles to characterize their magnetic properties from the microscopic level.

FePt nanoparticle samples were prepared by the wet chemical method. Precursor fcc FePt nanoparticles were prepared according to the method of Sun et al~ and were subsequently coated by SiO$_2$ according to the method of Fan et al~. Thus during the heat treatment thermal diffusion of Fe and Pt atoms was confined inside the SiO$_2$ nanoreactor. For details of the fabrication process, we refer the reader to Yamamoto et al~. For the XMCD measurements, the nanoparticle samples were supported by silver paste on a sample holder. After the preparation of the samples, they were kept in an Ar atmosphere in order to prevent oxidation until the XMCD measurements. XAS $\mu(\mu_+ + \mu_-)/2$ and XMCD $\mu_+ - \mu_-$ spectra were obtained at the helical undulator beam line BL23SU of SPring-8. Here, $\mu_+$ and $\mu_-$ are XAS spectra taken with the light helicity parallel and antiparallel to the incident photon direction, respec-
FIG. 1. (Color online) XAS and XMCD spectra at the Fe $L_{2,3}$ edges of the SiO$_2$-coated FePt nanoparticles under the applied magnetic field of 9 T. All the spectra have been normalized to the $L_3$ XAS peak intensity. Inset shows a schematic figure of the FePt nanoparticle coated by SiO$_2$. According to transmission electron microscopy (TEM) pictures reported by Yamamoto et al., the average size of the FePt nanoparticles is estimated to be 6-7 nm and that of the SiO$_2$ coat to be 10-15 nm.

Figure 1 shows the XAS and XMCD spectra at the Fe $L_{2,3}$ edges of the FePt nanoparticles. All the spectra have been normalized to the $L_3$ XAS peak intensity. Unlike the Fe $L_{2,3}$ spectra of FePt by Boyen et al. and Dmitrieva et al., each of the $L_3$ and $L_2$ edges exhibits a doublet structure: The $L_3$ doublet peaks are located at 707.7 eV and 709.3 eV, and the $L_2$ ones at 720.8 eV and 722.7 eV. Furthermore, broad shoulder/tail structures are observed on the high-energy side of the $L_3$ peak from 710 eV to 717 eV and on the high-energy side of the $L_2$ peak from 722 eV to 730 eV. We consider that the origin of the doublets is overlapping signals of FePt (at 707.7 and 720.8 eV) and Fe oxides (at 709.3 and 722.7 eV). The oxides are most likely extrinsic Fe$^{3+}$ oxides formed at the surface of bare FePt particles whose SiO$_2$-coating was removed when grinding the sample into fine powders, as one can see from the TEM picture [shown in Fig. 2(b) of Yamamoto et al.]. We tentatively attribute the shoulder/tail structures to the charge-transfer $2p^6d^5\rightarrow 2p^5d^7L_{sat}$ of the Fe$^{3+}$ oxide but the exact origin of the structure remains to be clarified. On the other hand, the lineshape of the experimental XMCD spectrum in Fig. 1 is almost identical to that of FePt by Dmitrieva et al. except for a small negative peak around 709 eV, indicating that contributions of the Fe oxides to the XMCD spectrum are small.

In order to estimate signals of the Fe oxides, we first subtracted the FePt XAS spectrum reported by Dmitrieva et al., where Fe oxide was completely removed by plasma treatment, from the experimental one. In Fig. 2(a), one can see that after having subtracted the FePt XAS spectrum multiplied by ~0.4, the spectral lineshape...
TABLE I. Values of spin ($M_{\text{spin}}$) and orbital ($M_{\text{orb}}$) magnetic moments (in units of $\mu_B$/Fe) and the coercive field $H_c$ (in units of T) for different FePt samples.

| Sample               | $M_{\text{spin}}$ | $M_{\text{orb}}$ | $M_{\text{orb}}/M_{\text{spin}}$ | $H_c$ |
|----------------------|-------------------|------------------|----------------------------------|-------|
| Nanoparticle (present work) | 1.4              | 0.12             | 0.08                             | 1.8   |
| Nanoparticle (gas phase) | 2.21             | 0.19             | 0.09                             | 0.038 |
| FePt thin films       | 0.5              | 0.025            | 0.05 ± 0.01                      | 0.1   |

became similar to that of BiFeO$_3$, where the Fe$^{3+}$ ion is located at the $O_h$ site, shown in the bottom of Fig. 2(a). Thus the intrinsic signals from FePt are estimated to be 40% of the total Fe L$_{2,3}$ XAS intensity. The experimental XMCD spectrum at the Fe L$_{2,3}$ edges of the FePt nanoparticles is shown in Fig. 2(b). The lineshape of the XMCD spectrum of FePt nanoparticles prepared by the gas condensation method by Dmitrieva et al. is also shown by a dotted curve. Unlike the XAS spectra, both XMCD data agree with each other except for the small negative peak around 709 eV in the present sample. From comparison of the present XMCD spectrum with the XMCD spectrum of BiFeO$_3$ shown at the bottom of Fig. 2(b), the small negative peak can be attributed to a peak of a Fe$^{3+}$ oxide. After having removed the Fe-oxide contributions from the experimental XAS and XMCD spectra, we applied the XMCD sum rules and obtained the spin moment $M_{\text{spin}} = 1.4 \mu_B$/Fe, the orbital moment $M_{\text{orb}} = 0.12 \mu_B$/Fe, and their ratio $M_{\text{orb}}/M_{\text{spin}} = 0.08$. These values are summarized in Table I and are compared with those of different kinds of FePt samples. The obtained $M_{\text{orb}}/M_{\text{spin}}$ ratio is comparable to the value (0.09) obtained for FePt nanoparticles prepared by gas phase condensation, and is larger than the values (~0.05) obtained for FePt thin films, indicating a high degree of $L_1_0$ order. The origin of this discrepancy is not clear at present, but the outermost layers of the bare FePt particles might also be oxidized to Fe$^{2+}$ and become non-ferromagnetic because the XAS and XMCD lineshapes of Fe$^{2+}$ oxides and metallic Fe are hardly distinguishable.

Figure 3(a) shows the Fe L$_3$-edge XMCD intensities of the FePt nanoparticles as functions of magnetic field at two different photon energies. The curve at $h\nu = 709.2$ eV, which reflects the XMCD signal of the Fe$^{3+}$ oxide, is linear in $H$ and shows no hysteretic behavior. Since the slope is given by the magnetic susceptibility $\chi$ of the Fe$^{3+}$ ion of the oxide, it is given by $C/T$ if the Fe$^{3+}$ ion is paramagnetic or by $C/T_N$ if it is antiferromagnetic. Here, $C$ and $T_N$ are the Curie constant for the Fe$^{3+}$ ($S = 5/2$) ion and the Néel temperature, respectively. From the slope $\chi \sim 0.023 \mu_B/T$, we estimated $T$ or $T_N \sim C/\chi = 325$ K, indicating that the Fe$^{3+}$ at 300 K are paramagnetic or slightly below $T_N$, and cannot be ferro/ferrimagnetic.

In contrast, the XMCD intensity at $h\nu = 707.7$ eV, which is dominated by FePt, shows a hysteretic behavior with $H_c$ of 1.8 T. Because a $M-H$ curve of the peak of the Fe oxides overlaps with the curve at $h\nu = 707.7$ eV, we obtained a $M-H$ curve of a ferromagnetic component by subtracting the curve at $h\nu = 709.2$ eV from the curve at $h\nu = 707.7$ eV. From the shape of the hysteresis loop thus obtained as shown in Fig. 3(a), one can see that the value of the remnant magnetization is half of that of the saturation magnetization and the shape itself is somewhat rounded compared to a typical rectangular hysteresis loop for ferromagnetic materials. These behaviors are characteristic of the hysteresis of the Stoner-Wohlfarth model, which explains $H_c$ based on the coherent reversal in non-interacting single-domain particles and in good agreement with some reports of nanopart-
Therefore, we first introduced the Stoner-Wohlfarth model with a fixed $H_c (= 2.5 \, \text{T})$ to reproduce the measured hysteresis loop, however, could not obtain a good fit as shown by a dashed curve in Fig. 3(b), because the experimental curve was broader in the high-field region. Then we assumed a distribution of $H_c$ over a finite range (we assumed the log-normal distribution) as shown in the inset of Fig. 3(b). The calculated hysteresis loop shown in Fig. 3(b) reproduces almost all the characteristics of the experimental curve, indicating that the SiO$_2$-coated FePt nanoparticles act as non-interacting single-domain particles whose $H_c$ is distributed from $\sim 1 \, \text{T}$ to $\sim 5 \, \text{T}$. The distribution of $H_c$ is possibly attributed to the distribution of structural defects of the FePt nanoparticles even though high degree of crystallinity is expected to be realized in the SiO$_2$-coated FePt nanoparticles as discussed below. Furthermore, because the Stoner-Wohlfarth model predicts $H_c = 0.48 H_{c(e)}$, where $H_{c(e)}$ is the $H_c$ for the magnetic field applied along the easy magnetization axis, the $H_{c(e)}$ of the present FePt nanoparticle sample is estimated as large as 3.75 T. This value is comparable to that of 4 T for FePt particulate films and larger than those of 2.2 T for FePt (001) dot arrays and 0.75 T for the microfabricated FePt (001) dots, indicating the large magnetocrystalline anisotropy of the SiO$_2$-coated FePt nanoparticles.

Finally, we discuss the origin of the observed large $H_c$ value for the SiO$_2$-coated FePt nanoparticles. The maximum single-domain size $R_{sd}$ is estimated as $R_{sd} \approx 9 \sqrt{\frac{k_B T_c}{2 \mu_0} K_{1c} / \mu_0 M_s^2}$, where $k_B$, $T_c$, $a_0$, $K_{1c}$, $\mu_0$, and $M_s$ are the Boltzmann constant, Curie temperature, lattice constant, anisotropy constant, vacuum permeability, and saturation magnetization, respectively. Using typical values for FePt nanoparticles of $K_{1c} \sim 10^7 \, \text{erg/cm}^3$, $a_0 = 0.386 \, \text{nm}$, and $M_s = 2.4 \, \mu_B/\text{Fe}$, we estimate the lower limit of $R_{sd}$ as $\sim 100 \, \text{nm}$, orders of magnitude larger than the particle size. Therefore, the SiO$_2$-coated FePt nanoparticles can form in single domains and hence obtain the large $H_c$. If defects are present in the nanoparticles, they hinder the single-domain formation because the defects act as nucleation centers. Thus, nucleation sites would lead to an enhancement of the $H_c$. In our fabrication method, the SiO$_2$ coating protects the small enough FePt nanoparticle from extra dispersion, deterioration, and oxidization during the sample preparation, leading to isolated single-domain FePt particles, and eventually to the large $H_c$ value.

In conclusion, we have investigated the spin and orbital magnetic moments of Fe in FePt nanoparticles coated with SiO$_2$ using XMCD measurements. The deduced ratio of the orbital to the spin magnetic moments $M_{orb}/M_{spin} = 0.08$ is nearly equal to that of FePt nanoparticles (0.09) condensed from gas phase for which oxidized layers were removed by in situ plasmas treatment. The magnetization measured by Fe L$_3$-edge XMCD was saturated around 6 T and $H_c$ was as large as 1.8 T, much larger than the $H_c$ ($\sim 0.038 \, \text{T}$) of the gas phase condensed samples, and consistent with the result of the SQUID measurement. The XMCD intensity versus magnetic field curve was fitted to the Stoner-Wohlfarth model for non-interacting single-domain nanoparticles whose $H_c$ is distributed between $\sim 1 \, \text{T}$ to $\sim 5 \, \text{T}$.

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