

Growth and atomic ordering of hard magnetic L1₀-FePt, FePd and CoPt alloy nanoparticles studied by transmission electron microscopy: alloy system and particle size dependence

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Atomic ordering of 10-nm-sized L1₀-FePt, FePd and CoPt nanoparticles have been studied by transmission electron microscopy and electron diffraction. Proceeding of the atomic ordering was confirmed by the increase of coercivity as well as electron diffraction. Among these three kinds of L1₀ nanoparticles, the atomic ordering reaction proceeded at the lowest temperature as low as 773 K for FePd nanoparticles. Coercivities of FePt and FePd nanoparticles largely increased with particle diameter and reached 10 kOe for 20-nm-sized FePt particles at room temperature. The large coercivity is attributed to the rotation magnetization of single-domain particles. For CoPt nanoparticles the observed coercivity was very small even after annealing at 1023 K for 1h. The slow rate of the L1₀ ordering can be attributed to the lowest T_c/T_m value in CoPt nanoparticles. L1₀ ordering was also confirmed even in very small FePt particles as small as 2-3 nm in diameter. By contrast, FePd nanoparticles with sizes less than 5 nm showed disordered fcc even after annealing at 873 K. The coercivity of 4-nm-sized L1₀-FePt nanoparticles were quite low and the observed largest coercivity was 490 Oe at 10 K after annealing at 873 K for 12 h.

Key words: L1₀ structure, FePt, FePd, CoPt, Nanoparticle, Large coercivity, TEM, Electron diffraction, Atomic ordering.

Introduction

Nanoparticles of equiatomic FePt, FePd, and CoPt ordered alloys have been attracting much interest for future ultra-high density magnetic storage media due to their large magnetocrystalline anisotropy energy [1], which enables a high thermal stability of magnetization against thermal fluctuations even in a very small particle. Different from the bulk or continuous film specimen, 10-nm-sized nanoparticles are single magnetic domains and the magnetization process is carried by rotation magnetization. According to the Stoner-Wohlfarth (SW) model [2], coercivity is expressed by the following relation:

$$H_c \approx \frac{K_u}{M_s} \quad (1)$$

where H_c represents the coercivity, K_u the uniaxial magnetoanisotropy constant and M_s the saturation magnetization. In this model, a random distribution of uniaxial magnetoanisotropy and coherent rotation of magnetization of single domain particles are assumed but interparticle magnetostatic interaction and thermal fluctuations of magnetization are not considered, hence these strict assumptions resulted in a limitation of this

model, that is, it is only valid in the case of magnetic particles with very strong magnetoanisotropy or at very low temperature. Recent experimental and theoretical progress has been published in review papers [3-5]. The latest computational model has treated both the magnetostatic and exchange interactions among the particles as well as the temperature effect, where these interactions and the temperature dependence of coercivity, remanence and switching field of magnetic particle assemblies have been clearly shown [6, 7]. Recently, it has been shown that the L1₀-type FePt nanoparticle behaves as a SW magnet by measurements of angular dependence of the irreversible switching field [8]. According to eq. (1), a very large coercivity, caused by the anisotropy energy, can be obtained by rotation magnetization in a single domain particle. The nano-sized L1₀-alloys have a large thermal stability of magnetization. For evaluating the thermal stability, the following equation is used [9]:

$$K_u V = k_B T \ln(f \cdot t_m) \quad (2)$$

where $k_B T$ represents the thermal energy, f the frequency factor (usually 10^9 s^{-1}) and t_m the measuring time. Considering the measuring time of 10^2 s , we deduce eq. (2) as

$$\frac{K_u V}{k_B T} = 25 \quad (3)$$

This equation (3) gives the critical particle volume from ferromagnetism to superparamagnetism due to the

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thermal fluctuation of magnetization. So it should be noted that a material with a very large K_u , ferromagnetism could be retained even in the case of very small particle sizes. The large K_u values of the $L1_0$ alloys have their origins in their tetragonal ordered structures with an alternative stacking of Fe (Co) (001) and Pt (Pd) planes along the [001] principal axis with respect to the fcc-lattice. The axial ratio (c/a) of these $L1_0$ alloys are reported to be 0.96-0.97, slightly smaller than unity due to the difference of atomic radii between Fe (Co) and Pt (Pd). The magnetic easy axis lies along the [001] c -axis of the $L1_0$ structure. Recently, a lot of reports have been published concerning the formation and hard magnetic properties of these $L1_0$ nanoparticles. One of the main topics in this field is a low temperature synthesis of the $L1_0$ phase in thin films or nanoparticles due to a technological request. In usual annealing, the $L1_0$ ordering in isolated nanoparticles requires a relatively high annealing temperature above 773 K. There are two recent developments in this topic, one is the addition of a ternary element [10] into FePt or CoPt alloy particles and the other is the alternative deposition of Fe/Pt films onto a heated substrate to enhance atomic diffusion [11]. Actually, for example, formation of the $L1_0$ structure around 573 K have been reported in the Fe/Pt multilayers [12, 13]. Among these recent reports on the $L1_0$ structures, there are differences in ordering temperature depending on the alloy system. The authors have studied FePt, FePd and CoPt oriented island-like nanoparticles in recent years and noticed that the $L1_0$ ordering temperature is the lowest in FePd nanoparticles. By contrast, CoPt nanoparticles need a higher annealing temperature than FePt or FePd. However, there is no report to compare the ordering rates of these three $L1_0$ alloy nanoparticles so far. In addition, our recent study revealed that the $L1_0$ ordering also depends on the particle size. Many studies have been reported on 10-nm-sized FePt particles with large coercivity at room temperature. Nowadays the interests have moved to the fabrication and characterization of smaller $L1_0$ particles with sizes less than 10 nm [14-16]. There are two problems to be solved in very small FePt nanoparticles for their application to magnetic storage media. One is a critical particle size for atomic ordering of the $L1_0$ particles, and the other is a superparamagnetic limit for the $L1_0$ nanoparticles. In order to solve these problems, fabrication of well-isolated $L1_0$ nanoparticles together with a homogeneous size distribution is necessary. To prevent the coalescence growth of particles during the post-deposition annealing for the $L1_0$ ordering, the authors have developed a fabrication process using a successive deposition of Pt (Pd) and Fe (Co) onto a heated single crystalline substrate for FePt or FePd nanoparticles formation [17, 18], where Pt (Pd) nanoparticles act as nucleation sites for successively deposited Fe particles and isolation of particles is ensured. Using

this technique we have tried to fabricate very small FePt and FePd nanoparticles with sizes less than 5 nm by reducing the deposited average thickness in the evaporation process.

In this study, the authors have fabricated 10-nm-sized $L1_0$ -FePt, FePd and CoPt nanoparticles, and their ordering rates have been discussed based on the melting point and the ordering energy. Following the $L1_0$ ordering is possible by monitoring the coercivity change as well as the structural change observed by transmission electron microscopy (TEM). In addition, atomic ordering in very small FePt and FePd nanoparticles were studied by TEM and also discussed were the size limit for the $L1_0$ ordering and magnetic properties of these smaller-sized particles.

Experimental

Specimen preparation was performed using an electron-beam evaporation apparatus (operated at 4 kV) with a base pressure of approximately 3×10^{-7} Pa. Pure Pd (99.95%), Pt (99.98%), Fe (99.97%), Co (99.99%) and Al_2O_3 (99.99%) crystals were used as evaporation sources. NaCl (001) and MgO (001) crystals were used as substrates. A quartz thickness monitor attached to the chamber was used to estimate the average thickness of the deposited layer. The evaporation process took advantage of the overgrowth of Fe (Co) on Pt (Pd) "seed" nanoparticles epitaxially grown on the cleaved NaCl (001) and/or MgO (001) substrates with a substrate temperature of 673 K [19]. Because of the large difference in the vapor pressures of Fe and Pt, it was difficult to control the alloy composition of specimens when we used an alloy target in the evaporation. After the deposition, an amorphous (a-) Al_2O_3 film was further deposited at the substrate temperature of about 623 K to protect the particles from oxidation and also to stabilize the particles in a separated condition. The average thickness (and the mean deposition rate) for Pd (Pt), Fe (Co) and Al_2O_3 were about 0.5-1.5 (0.5), 0.5-1.5 (0.5) and 4-10 nm (2 nm/min), respectively. According to energy dispersive x-ray spectroscopy (EDS) attached to TEM, the mean compositions of the present specimens were found to be nearly equiatomic compositions of Fe-50-56 at%Pt, Fe-49-58 at%Pd and Co-45-54 at%Pt. Heat treatments of the as-deposited nanoparticles (hereafter, expressed as Fe/Pt, Fe/Pd, and Co/Pt) for the formation of the ordered $L1_0$ nanoparticles were made in a high-vacuum furnace ($< 2 \times 10^{-5}$ Pa) at 673-1023 K for 1-24 h in an Al_2O_3 boat. The heating rate was about 5 K/min. After annealing, the specimen was gradually cooled down to the room temperature in the vacuum furnace with a mean cooling rate of about 10 K/min. Specimen films grown on the NaCl substrate were annealed at temperatures below 873 K. The as-deposited and annealed films were removed from the NaCl substrate by immersing

the substrate in distilled water, and were mounted onto copper grids for TEM observations with transmission electron microscopes operated at 200 kV (JEOL, JEM-2010) and 300 kV (JEOL, JEM-3000F). TEM observations of specimen films after annealing on Cu grids without the NaCl (001) substrate were also performed. These TEM specimens were prepared by annealing the as-deposited films on Cu grids after removing them from the substrate. For an in-situ TEM observation of the atomic ordering, a specimen heating stage was used. Elemental analysis was performed using EDS. Magnetic properties of the $L1_0$ nanoparticles on the MgO (001) and NaCl (001) substrates after the heat-treatments were measured using a SQUID magnetometer (Quantum Design, MPMS-5S) in the temperature range between 10 and 400 K.

Results and Discussion

Growth and atomic ordering of 10-nm-sized $L1_0$ particles

Successive deposition of Pt and Fe onto NaCl substrate resulted in the formation of nano-complex island-like particles of bcc-Fe and Pt with a 2-dimensional dispersion. Because of the epitaxial growth of Pt and Fe on the heated (673 K) single crystalline substrate, there are mutually fixed orientation relationships

between the NaCl substrate and Pt, and between Pt and Fe as follows [15]: $[011]_{\text{NaCl}} \parallel [011]_{\text{Pt}}$, $(100)_{\text{NaCl}} \parallel (100)_{\text{Pt}}$, and $[100]_{\text{Pt}} \parallel [100]_{\text{Fe}}$, $(010)_{\text{Pt}} \parallel (011)_{\text{Fe}}$, respectively. A post-deposition annealing at temperatures higher than 773 K lead to the formation of the $L1_0$ ordered phase within each nanoparticle. Figure 1(a) shows the TEM image of $L1_0$ -FePt nanoparticles after annealing at 873 K for 1 h. Island-like 10-nm-sized FePt particles are dispersed and separated from each other by a- Al_2O_3 thin film. A selected area electron diffraction (SAED) pattern revealed the (001) orientation of these $L1_0$ nanoparticles as shown in Fig. 1(b), where superlattice reflections are clearly seen. High-resolution TEM (HREM) observation indicated an existence of a variant-domain structure [17, 19] in these FePt particles as shown in Fig. 1(c). The variant-domain structure of the $L1_0$ -FePt nanoparticles was composed of three-kinds of crystallographic domains with three-kinds of orthogonal c-axes orientation. These variant-domain structures disappeared and single crystal particles appeared after a prolonged annealing at 873 K for 24 h [20]. Particle structure and morphology of CoPt nanoparticles are similar to those of FePt. Figure 2(a), 2(b) and 2(c) show a TEM image, the corresponding SAED pattern and a HREM image of Co-54 at%Pt nanoparticles after annealing at 973 K for 1 h. Superlattice reflections clearly visible in the SAED

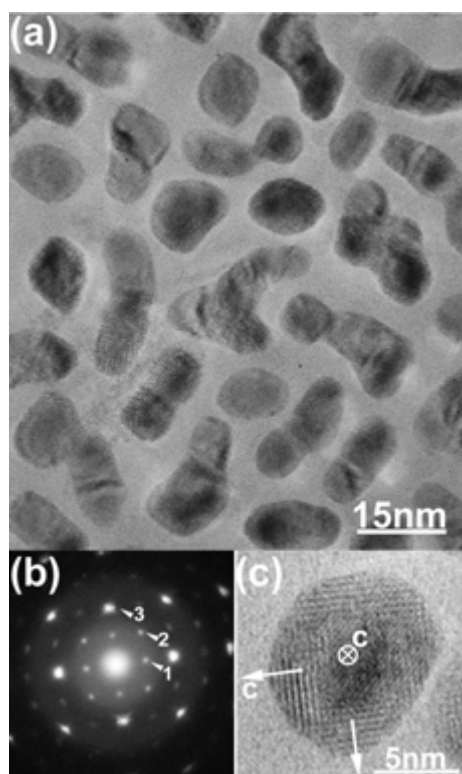


Fig. 1. TEM image, corresponding SAED pattern and HREM image of FePt nanoparticles after annealing for 1 h at 873 K. Mean alloy composition was Fe-50 at%Pt. Indices of reflections marked by arrows are as follows: 1. 001FePt (from a-domain), 2. 110FePt (from c-domain) and 3. 020FePt.

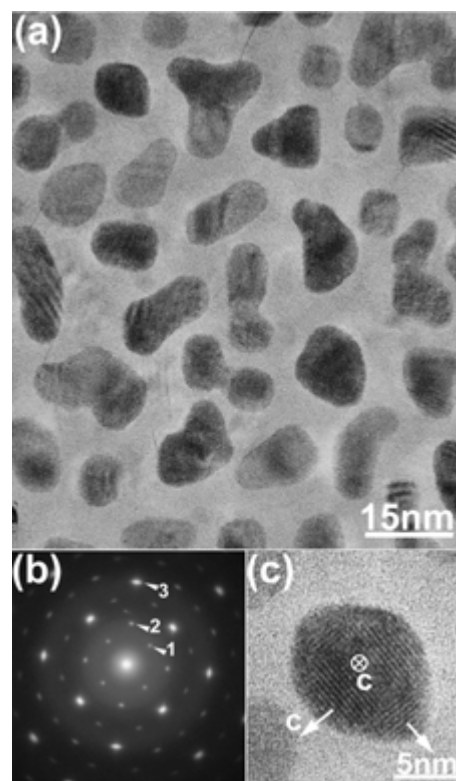


Fig. 2. TEM image, corresponding SAED pattern and HREM image of CoPt nanoparticles after annealing for 1 h at 973 K. Mean alloy composition was Co-54 at%Pt. Indices of reflections marked by arrows are as follows: 1. 001CoPt (from a-domain), 2. 110CoPt (from c-domain) and 3. 220CoPt.

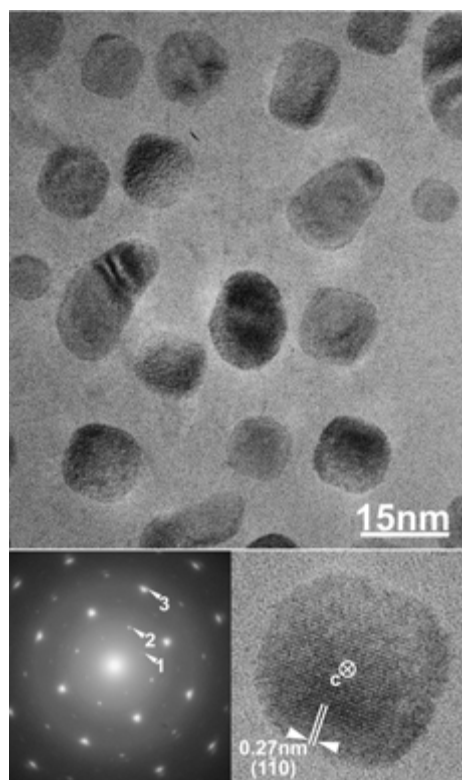


Fig. 3. TEM image, corresponding SAED pattern and HREM image of FePd nanoparticles after annealing for 1 h at 873 K. Mean alloy composition was Fe-57 at%Pd. Indices of reflections marked by arrows are as follows: 1. 001FePd (from a-domain), 2. 110FePd (from c-domain) and 3. 220FePd.

pattern and the variant-domain structure of the tetragonal ordered phase indicate the atomic ordering just the same as in the case of FePt nanoparticles. As we stated above, both FePt and CoPt nanoparticles possess a similar tendency regarding their particle morphology and structure. By contrast, it was found that single crystalline (single variant) nanoparticles were directly formed in FePd nanoparticles after annealing at 773 K for 1 h [18]. Figure 3(a), 3(b) and 3(c) show a TEM image, the corresponding SAED pattern and a HREM image of the Fe-57 at%Pd nanoparticles after annealing at 873 K for 1 h. The HREM observation revealed that there were two kinds of c-axis orientation for the single crystalline FePd nanoparticles, one with the c-axis oriented normal to the film plane and the other parallel to the film plane, but the population of nanoparticles with their c-axis oriented normal to the film plane was larger in number than those oriented parallel to the film plane [21]. Compositional analyses of these nanoparticles using nano-beam EDS indicated the existence of an alloy composition distribution from particle to particle, but all compositions analyzed were included within the $L1_0$ phase region. Our 10-nm-sized $L1_0$ particles are all magnetically single domains since limiting sizes for single-magnetic domains are 340, 610 and 200 nm for $L1_0$ -FePt, CoPt and FePd alloys, respectively [1].

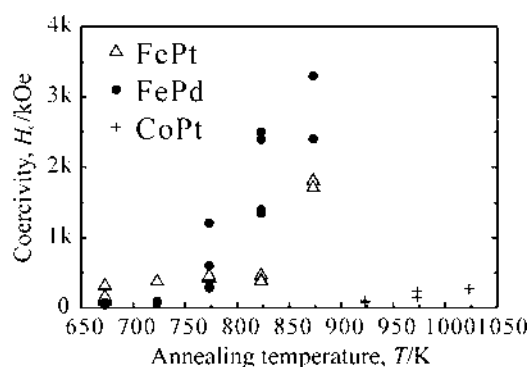


Fig. 4. Annealing temperature dependence of room temperature coercivity for 10-nm-sized FePt, FePd and CoPt nanoparticles. Annealing time for all specimens was 1 h. Above 773 K, a large increase of coercivity was observed. The coercivity shown in this figure includes both perpendicular and in-plane results.

Atomic ordering and hard magnetic property

The annealing temperature dependence of the coercivity for 10-nm-sized FePt, FePd and CoPt nanoparticles is shown in Fig. 4 in the temperature range between 673 and 1023 K. The annealing time was set to be 1 h to compare the ordering rate of these three kinds of $L1_0$ nanoparticles. A large coercivity exceeding 1 kOe was obtained for FePd nanoparticles after annealing at 773 K, which was the lowest annealing temperature among these three kinds of $L1_0$ nanoparticles. The coercivity increased with annealing temperature and reached 3.5 kOe after annealing at 873 K. The coercivity of FePt nanoparticles exceeded 1 kOe after annealing at 873 K. These large increases of coercivity can be attributed to the $L1_0$ phase formation with large magnetocrystalline anisotropy constant. Different from the FePt or FePd nanoparticles, CoPt nanoparticles showed a very small coercivity even after annealing at 923–1023 K where the $L1_0$ phase formation was confirmed by SAED and HREM. The rate of atomic ordering towards the $L1_0$ structure formation in these three kinds of alloy nanoparticles was found to be quite dependent on the alloy system. In order to reveal the reason for the differences of the temperature dependence of the coercivity, annealing temperatures for these three kinds of alloys were normalized by their melting temperatures as shown in Fig. 5, since the normalized temperature can be related to the diffusion coefficient via vacancy concentration which plays an important role in bulk diffusion mechanism for the $L1_0$ ordering. This means that an alloy system with a lower melting temperature possesses a relatively higher thermally equilibrium vacancy concentration. As a result, coercivities for both of the FePt and FePd increased at about $0.4T_m$ [21], while it was found that the annealing temperature dependence of the coercivity for CoPt nanoparticles could not be explained by the vacancy concentration. Then we compared the ordering processes together with the hard magnetic properties from the viewpoint of the

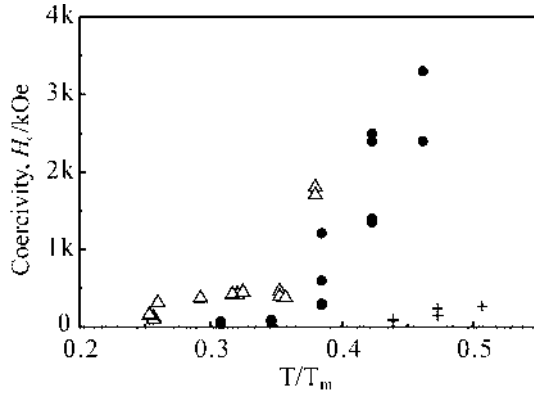


Fig. 5. Normalized annealing temperature dependence of coercivity reproduced from Fig. 4. The coercivity for both FePt and FePd increased at annealing temperatures higher than $0.4 T_m$.

order-disorder transition temperature, which is related to the ordering energy. Based on the Bragg-Williams (BW) theory [22], the following relation between the degree of order (S), order-disorder transition temperature (T_c) and ordering energy (v) are derived:

$$S \frac{T_c}{T} = \frac{1}{2} \log \left(\frac{1+S}{1-S} \right) \quad (4)$$

$$T_c = -\frac{4v}{k_B} \quad (v < 0) \quad (5)$$

According to eq. (5), it is found that a specimen with a higher T_c possesses the larger ordering energy within a qualitative consideration, although the BW theory is invalid in the case of FCC-L1₀ first order transition because it does not take second nearest neighbor interactions of atoms into consideration. Then we define a parameter T_c/T_m in order to compare the ordering process of the three kinds of the L1₀ nanoparticles, where an alloy system with higher T_c/T_m is thought to order more easily. As a result, T_c/T_m of 0.828, 0.606 and 0.550 were obtained for FePt, FePd and CoPt alloys, respectively [23]. This result qualitatively reflects the experimental result of slow ordering in the CoPt system.

In order to examine the way the atomic ordering reaction proceeds, we measured diffracted beam intensity profiles for FePt, FePd and CoPt nanoparticles from the corresponding SAED patterns. Figure 6 shows the intensity profiles of 220 reflection measured along the $[110]^*$ direction in reciprocal space from SAED patterns for Fe-50 at%Pt (873 K-1 h annealing), Fe-57 at%Pd (873 K-1 h annealing) and Co-46 at%Pt (973 K-1 h annealing) nanoparticles. Because of the formation of the tetragonal ordered phase and also the epitaxial growth of nanoparticles, splitting of 220 and 202 (and/or 022) reflections must appear in the profiles. Actually, in the case of FePt and FePd specimens, shoulders due to the 202 (022) reflection appeared at around 7.6 nm^{-1} , indicating that the L1₀ ordering reaction is

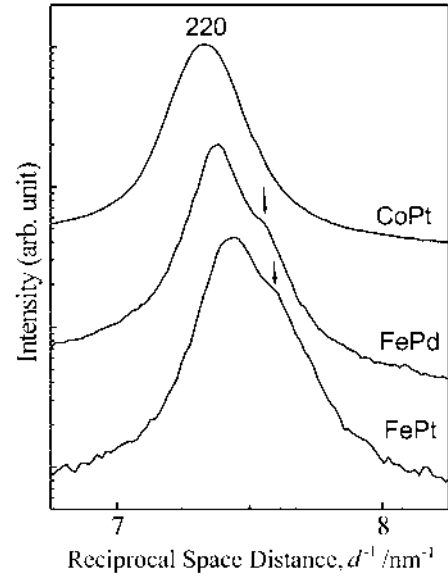


Fig. 6. Diffracted beam intensity profiles for 220 fundamental reflections of 10-nm-sized FePt, FePd and CoPt nanoparticles. Annealing condition was 873 K for 1 h (FePt, FePd) and 973 K for 1 h (CoPt). A shoulder from 202 and / or 022 reflection due to the tetragonal ordered structure can be seen in the case of FePt and FePd nanoparticles, while there is no splitting of the 220 reflection of CoPt specimen, indicating insufficient ordering even after annealing at 973 K.

proceeding in these specimens. However, there is no splitting in the 220 reflection for CoPt nanoparticles. So it is concluded that the rate of ordering via diffusion in CoPt nanoparticles is very slow compared to those for FePt or FePd. Chen *et al.* [24] have reported a coercivity as large as 14 kOe in their CoPt nanoparticles after annealing at 953 K for 100 h. They stated that a specimen after annealing at 873 K for less than 7 h did not show such a large coercivity and no superlattice reflections were observed in the x-ray diffraction pattern, also indicating the slow ordering process in CoPt alloy nanoparticles.

Before moving to next section, it should be noted that our successive deposition process does not cause any delay of the atomic ordering reaction, since recent reports on sputter-deposited FePt granular film indicated the necessity of annealing at as high a temperature as 873-973 K for the L1₀ ordering [25, 26], although Fe and Pt were co-deposited onto a substrate simultaneously in the sputtering process.

Particle size dependence of coercivity

The coercivity for the L1₀-FePt and FePd nanoparticles with different average sizes are shown in Fig. 7. Solid and dotted lines indicate the theoretically-derived size dependence of the coercivity for FePt and FePd nanoparticles, respectively. The calculation was performed using Pfeiffer's equation [27] assuming a random orientation of non-interacting particles and considering the thermal effect on coercivity expressed

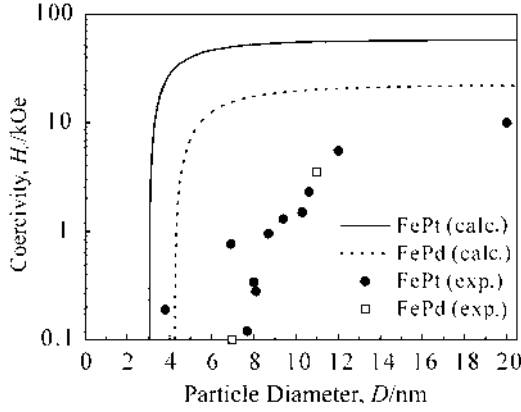


Fig. 7. Particle size dependence of room temperature coercivity for FePt and FePd nanoparticles. Solid and dotted lines indicate the calculated coercivity based on Pfeiffer's equation assuming a magnetocrystalline anisotropy constant for fully ordered bulk FePt and FePd magnets, respectively.

as follows:

$$H_c = 0.96 \frac{K_u}{M_s} \left[1 - \left(\frac{V_s}{V} \right)^{0.77} \right] \quad (6)$$

$$V_s = \frac{25k_B T}{K_u} \quad (7)$$

where the volume for the superparamagnetic limit is denoted by V_s . The relaxation frequency was assumed to be 10^9 s^{-1} and the thermal relaxation time of spins is set to be 10^2 s [9]. In the calculations, we used a K_u of $7 \times 10^6 \text{ J/m}^3$ and $2.6 \times 10^6 \text{ J/m}^3$ as the values for bulk

FePt [28] and FePd [29], respectively. The measured coercivity drastically decreased with particle diameter reduction, which can be attributed to an increase of thermal fluctuations and/or a decrease of the long-range order parameter with a decrease in the particle size. Actually, according to our previous results, remanent magnetization decay was found in 12-nm-sized FePt nanoparticles [30] and also revealed that the degree of order was relatively low ($S = 0.55$) [31] even after an annealing at 873 K for 24 h. Although the size dependence of coercivity shown in Fig. 7 can be explained qualitatively from the above reasons, the experimentally-obtained coercivity in each $L1_0$ -alloy was much smaller than that predicted by theoretical calculation. In Pfeiffer's equation, we assumed K_u as that of a fully ordered bulk $L1_0$ magnet. However, the magnetocrystalline anisotropy constant depends on the degree of order [32-34], so it is presumed that K_u of the $L1_0$ nanoparticles with a low degree of order must be small compared to that of the fully ordered state. The relation between K_u and the degree of order was investigated by using FePt thin films [33, 34], where large decreases of K_u were reported when the degree of order decreased. Magnetostatic interaction energy among the nanoparticles is thought to be much smaller than the anisotropy energy considering the very large K_u values of $L1_0$ -FePt or FePd. However, for nanoparticles with small particle sizes less than 10 nm, K_u will decrease due to the decrease of the degree of order. In such a situation, magnetostatic interaction which is not included in the eqs. (6) and (7) may play an important

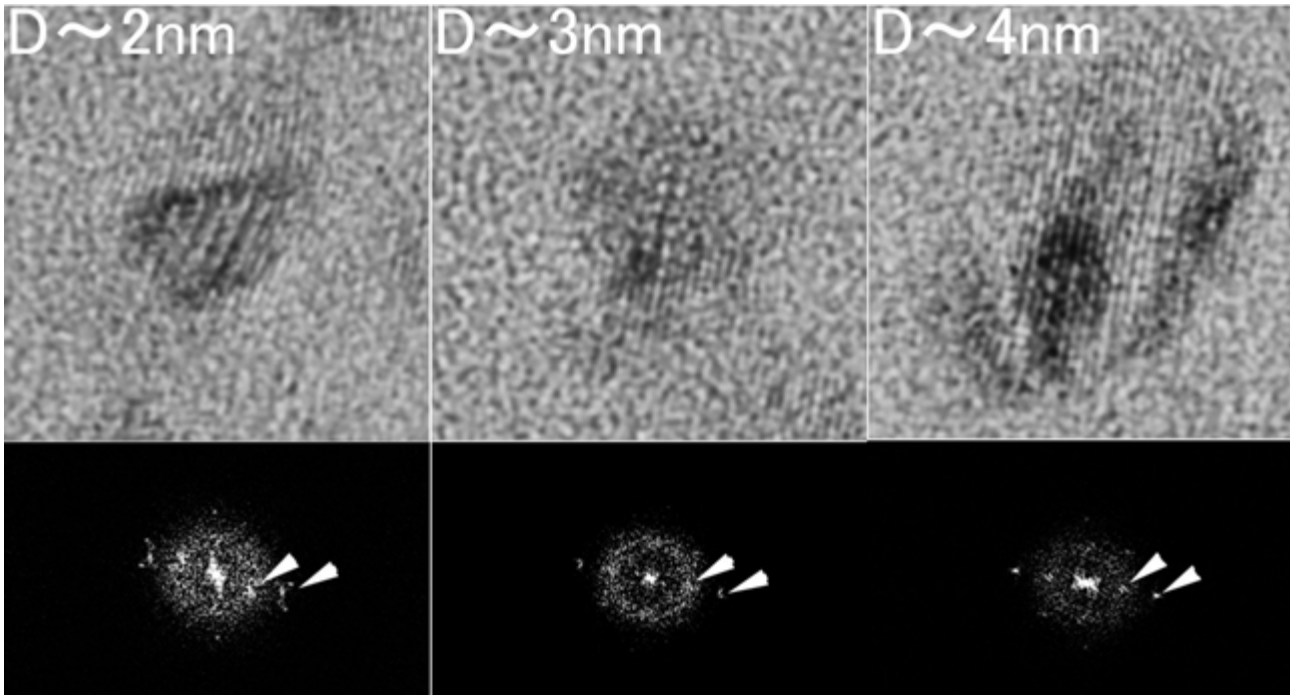


Fig. 8. HREM images and the corresponding FT patterns for FePt nanoparticles with diameters of 2, 3 and 4 nm. Lattice fringes of (001) plane are clearly seen even in 2-nm-sized particles.

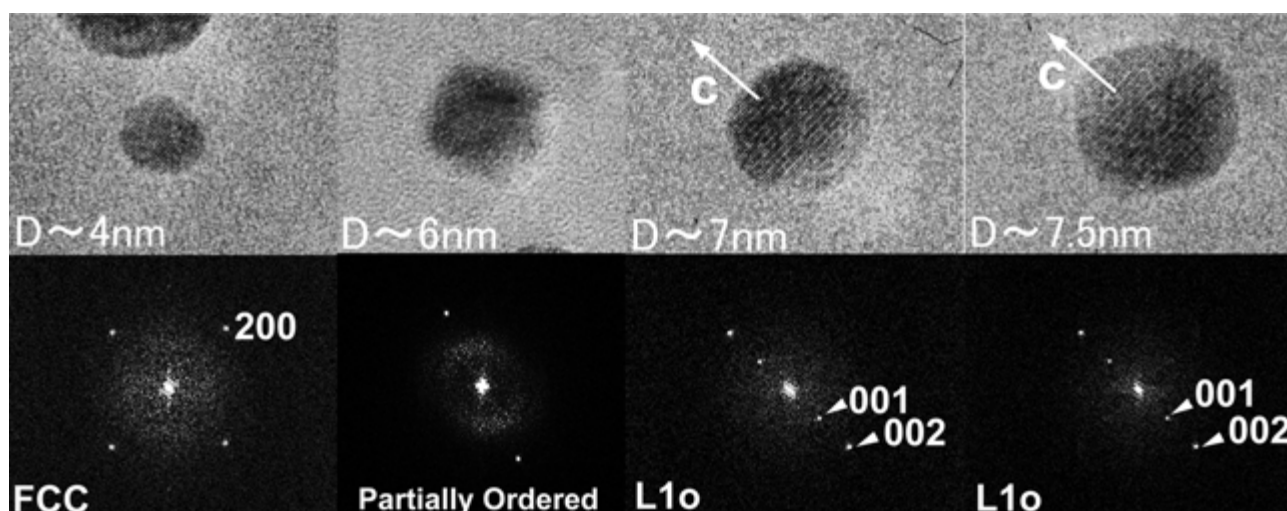


Fig. 9. HREM images and the corresponding FT patterns for FePd nanoparticles with diameters of 4, 5.6, 6.7 and 7.5 nm. Clear superlattice reflections are seen for particles of 6.7 and 7.5 nm in diameter. $L1_0$ lattice fringes are partially observed in 5.6 nm FePd nanoparticles where diffuse scattering was observed in the FT pattern. No superlattice reflections are observed in 4-nm-sized nanoparticles.

role in the coercivity. According to a recent theoretical study [7], coercivity changes with the strength of the magnetostatic interaction among the particles.

Particle size dependence of the $L1_0$ ordering

In order to examine the particle-size dependence of the $L1_0$ ordering, we fabricated FePt and FePd nanoparticles with sizes less than 10 nm by reducing the deposited thickness. By decreasing the particle size below 7 nm in diameter, the $L1_0$ phase formation was promoted in the as-deposited condition deposited at 673 K [35]. Figure 8 shows HREM images and the corresponding Fourier Transform (FT) patterns for 2-4-nm-sized FePt nanoparticles. Lattice fringes of the (001) lattice planes of the $L1_0$ structure are clearly seen in these images, and 001 superlattice reflections in the FT patterns also indicate the $L1_0$ ordering. Then we also fabricated smaller sized FePd nanoparticles. HREM observation revealed the clear atomic ordering in FePd particles with sizes larger than 6 nm, and by contrast the 4-nm-sized particle had a disordered fcc structure after annealing at 873 K for 1 h. Lattice fringes of (001) planes were partially observed in a 5-nm-sized FePd nanoparticle. These HREM images and the FT patterns shown in Fig. 9 indicate the existence of the size limit for the $L1_0$ ordering in the present FePd nanoparticles to be around 5 nm in diameter. Disordered Fe-Pd nanoparticles with sizes of 2-4 nm have been reported after annealing at as high a temperature as 920 K [36].

Room temperature magnetization curves for the 4-nm-sized FePt particles are shown in Fig. 10(a) (as-deposited), 10(b) (873 K-1 h) and 10(c) (873 K-10 h). All specimens showed ferromagnetism at room temperature, though the coercivities were less than 200 Oe in spite of the $L1_0$ ordering in the annealed specimens. Magnetization curves for FePd nanoparticles with a

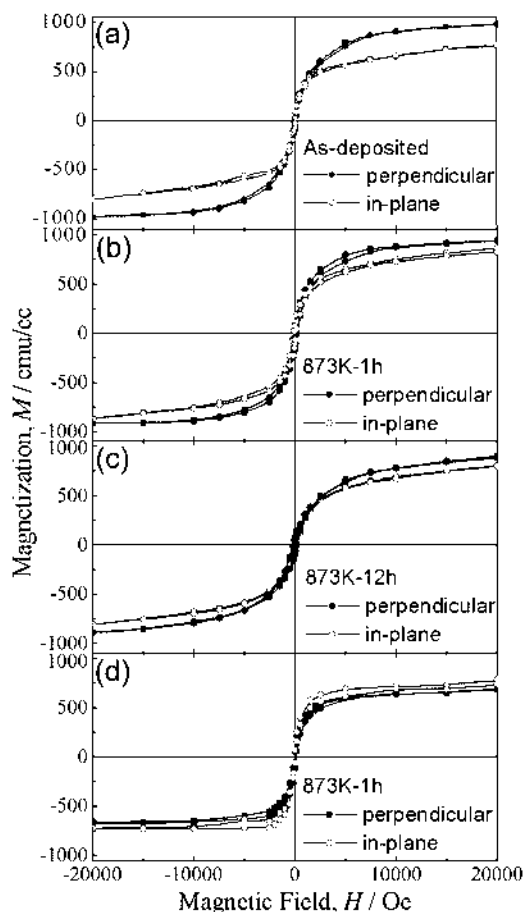


Fig. 10. Magnetization curves measured at 300 K for FePt nanoparticles (as-deposited: 10 (a), 873 K-1 h annealed: 10 (b), 873 K-10 h annealed: 10 (c) and FePd nanoparticles after annealing at 873 K-1 h (10 (d)).

mean size of 7 nm showed a similar tendency with a small coercivity (100 Oe) as shown in Fig. 10(d). The annealing temperature dependence of the coercivity for

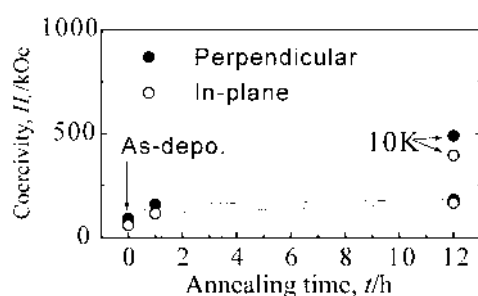


Fig. 11. Coercivity change on annealing at 873 K for 4-nm-sized FePt nanoparticles. In spite of the long-time annealing at 873 K, the largest coercivity obtained remained 490 Oe at 10 K.

the FePt particles is shown in Fig. 11. The coercivity at room temperature increased a little during the long-time annealing at 873 K and remained only 180 Oe after annealing for 12 h. This tendency indicates that the ordering reaction proceeded a little at 873 K in the case of 4-nm-sized FePt particles. The coercivity at 10 K also remained small (490 Oe) in spite of the $L1_0$ ordering. According to Pfeiffer's equation, the critical size for superparamagnetism of the $L1_0$ FePt and FePd particles are estimated to be 3 and 4.2 nm in diameter, respectively, assuming a spherical shape with bulk K_u values [28, 29].

Conclusions

Epitaxially grown $L1_0$ -type FePt, CoPt and FePd nanoparticles were fabricated by electron beam deposition and post-deposition annealing at temperatures higher than 773 K. A large coercivity exceeding 1 kOe at room temperature was obtained after annealing for 1 h at 773 K and 873 K for FePd and FePt nanoparticles, respectively. The difference in ordering temperature between FePd and FePt can be explained by the difference in melting temperatures between them, that is, annealing temperatures for getting large coercivities normalized by the melting temperatures corresponding to about $0.4 T_m$ for both of these alloys. The normalized annealing temperature qualitatively reflects the diffusion coefficient via vacancy concentration. The coercivity of CoPt nanoparticles remained quite low around 240 Oe even after annealing at 1023 K for 1 h, although clear superlattice reflections appeared in the corresponding SAED pattern. A diffracted beam intensity profile for the CoPt nanoparticles revealed that there was no splitting of 220 and 202 (and/or 022) reflections, indicating insufficient $L1_0$ ordering. The observed slow ordering process can be attributed to the lowest value of T_c/T_m among these three kinds of $L1_0$ nanoparticles, since T_c and $1/T_m$ reflects the ordering energy and the vacancy concentration relative to the annealing temperature, respectively. The coercivities of FePt and FePd nanoparticles largely increased with particle diameter and reached 10 kOe for 20-nm-sized FePt particles at room temperature. This large coerci-

vity is attributed to the rotation magnetization of single-domain particles, however, the observed coercivities were much smaller than those predicted by Pfeiffer's model considering thermal effects. The coercivity strongly depends on the degree of order via magnetocrystalline anisotropy as well as particle volume.

$L1_0$ ordering was also confirmed even in very small FePt particles as small as 2-3 nm in diameter. By contrast, FePd nanoparticles with sizes less than 5 nm showed a fcc disordered phase after annealing at 873 K. Magnetization curves for 4-nm-sized FePt and 7-nm-sized FePd nanoparticles showed very small coercivities in spite of the $L1_0$ ordering.

The successive deposition method presented in this study is suitable for fabricating both well-oriented and well-isolated $L1_0$ nanoparticles, however, high temperature annealing is necessary for the $L1_0$ ordering. The ordering temperature must be decreased when we consider an application of these $L1_0$ nanoparticles to high-density storage media. Addition of a ternary element into these alloys and sputtering of multilayered films onto a heated substrate are well-known techniques to reduce the ordering temperature. However, the role of additives is still an open question. A novel method to synthesize $L1_0$ nanoparticles at reduced temperature as well as good orientation, good isolation and a high-density packing of particles is necessary for further progress in this field. The effects of purity of target materials and vacuum pressure during the evaporation on the $L1_0$ ordering must be examined also in detail.

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