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# Magnetic anisotropy in spherical $\text{Fe}_{16}\text{N}_2$ core-shell nanoparticles determined by torque measurements

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The magnetic anisotropy energy for core-shell  $\alpha''\text{-Fe}_{16}\text{N}_2$  nanoparticles was evaluated by the rotational hysteresis loss obtained from magnetic torque measurements. The saturation magnetization of the  $\alpha''\text{-Fe}_{16}\text{N}_2$  core was deduced from volume fractions of  $\alpha''\text{-Fe}_{16}\text{N}_2$  determined by an analysis of a low-temperature Mossbauer spectrum. The saturation magnetization and the anisotropy energy were found to be 234 emu/cc and 6.9 Merg/cm<sup>3</sup>, respectively. These values coincide with those of bulk-like single-phase  $\alpha''\text{-Fe}_{16}\text{N}_2$  particles. This crystalline anisotropy is still smaller than the shape anisotropy of the thin films ( $2\pi Ms^2 = 20$  Merg/cm<sup>3</sup>), and a perpendicular magnetic state is not expected for the thin-film form. © 2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). [<http://dx.doi.org/10.1063/1.4974276>]

## I. INTRODUCTION

Fe nitrides have a variety of crystalline structures corresponding to the concentration of nitrogen. There are a few ferromagnetic nitrides, and many of these have been studied from the viewpoint of magnetic materials.<sup>1,2</sup> Early-stage efforts for developing magnetic materials focused on applications for magnetic recording tape media using  $\text{Fe}_4\text{N}$  pigments<sup>3</sup> and recently as a candidate for a spintronics material with a half-metallic electronic structure.<sup>4</sup>  $\alpha''\text{-Fe}_{16}\text{N}_2$  has a tetragonally distorted structure, in which one of the  $\langle 100 \rangle$  axes is elongated and the nitrogen atoms are ordered. This substance has been studied by many for its high saturation magnetization;<sup>5,6</sup> the compound also exhibits a uniaxial magnetic anisotropy<sup>7,8</sup> due to the distorted structure, showing promise for use in applications such as high-performance magnetic data recording tapes<sup>9</sup> with core-shell type spherical nanoparticles (NPs).<sup>10</sup> Recently, new permanent magnet materials that do not require rare elements have been highly sought, and a number of ferromagnetic substances with high transition temperatures have been proposed as potential candidates for the same.<sup>11</sup>  $\alpha''\text{-Fe}_{16}\text{N}_2$  is a good candidate, as it has high saturation moments and a large anisotropy constant ( $K_u$ ). The amplitude of  $K_u$  is an important parameter not only for bulk applications<sup>12</sup> but also for the realization of perpendicular magnetic thin films. We have reported that the  $K_u$  of the core-shell  $\alpha''\text{-Fe}_{16}\text{N}_2$  NP, estimated from typical torque measurements, is  $4.4 \times 10^6$  erg/cm<sup>3</sup>.<sup>10</sup>

Detailed torque measurements were performed to obtain a more precise value of  $K_u$  for  $\alpha''\text{-Fe}_{16}\text{N}_2$ . Because the NPs have a core-shell type structure, where a nonmagnetic oxide layer covers the  $\alpha''\text{-Fe}_{16}\text{N}_2$  cores, the low-temperature Mossbauer spectra were analyzed to estimate the magnetization of this portion of the  $\alpha''\text{-Fe}_{16}\text{N}_2$  cores from the ratio of nitrides and oxides, and  $K_u$  was deduced from these values.

## II. EXPERIMENTAL

$\alpha''\text{-Fe}_{16}\text{N}_2$  NPs were prepared using  $\text{NH}_3$  nitrification. First,  $\text{Fe}_3\text{O}_4$  particles with a diameter of 18 nm underwent hydrogen reduction at 450 °C for 4 h. Succeeding nitrification was carried out at

temperatures between 150 and 170 °C in an atmosphere of H<sub>2</sub> and NH<sub>3</sub>.<sup>13</sup> Sample characterization was performed using X-ray diffraction (XRD) and transmission electron microscopy (TEM).<sup>10</sup> Magnetically aligned samples were prepared by drying the organic solvent of particles on the polymer films in a magnetic field parallel to the films.

The magnetization and magnetic torque were measured at room temperature (defined in our study as 300 K) using a SQUID magnetometer, a vibrating sample magnetometer and an automatic torque meter, respectively. Torque curves were measured under an external magnetic field of up to 22 kOe and the torques were measured by rotating the external field in the clockwise and counterclockwise directions. Rotational hysteresis of the torque was evaluated from the area drawn by the rotation under an external field ranging from 0.5 kOe to 10 kOe. Mössbauer spectra were recorded at sample temperatures of 300 K and 4.2 K. The velocity and isomer shift were calibrated to those of natural Fe foil at room temperature. Film samples were used for magnetic and Mössbauer measurements. Data fitting was carried out using MossWinn 4.0, a commercially available program.

### III. RESULTS AND DISCUSSION

The structural characterization of the obtained  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> NPs was described in a previous paper.<sup>10</sup> The particles maintained their spherical shapes between the starting state and post nitrification. The averaged particle size was approximately 20 nm, and the TEM photo<sup>9</sup> showed a core-shell structure with a crystalline  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> core and a shell probably composed of amorphous-like iron oxide (hereafter referred as Fe-O). As mentioned below, Mössbauer spectroscopy found the outer shell had an Fe<sup>3+</sup> state, therefore the chemical formula of the outer shell is considered to be Fe<sub>2</sub>O<sub>3</sub> rather than Fe<sub>3</sub>O<sub>4</sub>.

Figure 1 shows the angular dependence of the magnetization curves. The maximum coercive force was measured as 3.5 kOe when the angle between the magnetization direction and the external magnetic field was 0°, and the squareness was found to be 0.89.<sup>13</sup> The saturation magnetization was calculated as 108 emu/g using the net weight of samples, including non-magnetic components, at room temperature.<sup>10</sup>

Mössbauer spectra reflect the local environments of Fe, enabling us to estimate the portion of magnetic iron atoms using the area ratio of the spectra. The area ratios from spectra recorded at low temperatures are more realistic due to the temperature dependence of recoil-free emission rates.<sup>14</sup> We recorded low-temperature spectra at 4.2 K, which are plotted in Fig. 2. The numerical fitting was performed under the condition that the spectrum consisted of four magnetically ordered sub spectra and one doublet. Three of the ordered sub-spectra coincided with a set of hyperfine sub-spectra of  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub>,<sup>15</sup> the sub-spectrum with a higher hyperfine field of 500 kOe is attributed to the Fe oxides.

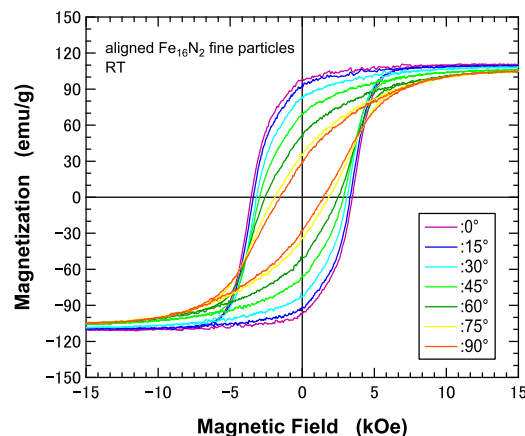


FIG. 1. Magnetization curves of the  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> aligned sample. The external magnetic field was applied with an angle from the magnetic alignment direction. The angle ranged from 0 to 90° and coercive fields decreased monotonically with an increase of the angle. Data were partly shown in a previous report.<sup>13</sup>

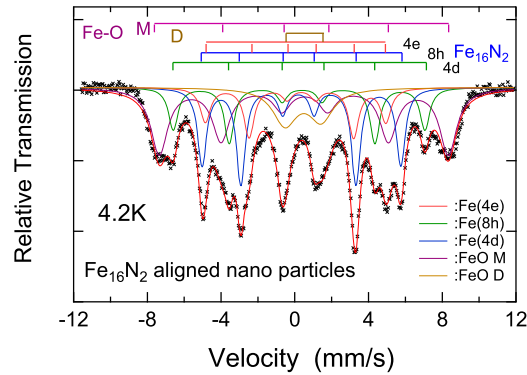


FIG. 2. Mossbauer spectrum for the  $\alpha$ -Fe<sub>16</sub>N<sub>2</sub> aligned sample recorded at 4.2 K. Solid lines show the results of the fit. Corresponding peak positions are indicated by three bars for magnetic subspectra of the  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> core and two bars, magnetic sextet (M), and paramagnetic doublet (D), for the outer shell of Fe oxides (Fe-O).

The fitting parameters at 4.2 K are listed in Table I. From this fitting, these oxides were paramagnetic at room temperature<sup>10</sup> and the corresponding subspectrum had an area ratio of 43.8% and an isomer shift of 0.38 mm/s, supporting that Fe atoms in the Fe-O shell had an Fe<sup>3+</sup> state.<sup>13</sup> Fe atoms belonging to  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> were found at a concentration of 54.4%, slightly less than that at room temperature, 56.2%.<sup>10,13</sup>

Consider that the sample consists of only Fe<sub>16</sub>N<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> and 1 g of the whole sample contains  $x$  mol of FeN<sub>1/8</sub> (1 mol = 57.6 g) and  $y$  mol of Fe<sub>2</sub>O<sub>3</sub> (1 mol = 80.0 g), respectively. The equations  $57.6x + 80.0y = 1$  and  $x/y = 54.4/46.5$  can be applied in this case. Solving these equations gives  $x = 0.00794$ ; therefore, 1 g of the whole sample contains 0.457 g of FeN<sub>1/8</sub>. From this result,  $M_s = 108$  emu/g of the whole sample can be converted to 234 emu/g, namely 1750 emu/cm<sup>3</sup>. If we consider Fe<sub>3</sub>O<sub>4</sub> as Fe-O, instead of Fe<sub>2</sub>O<sub>3</sub> for reference, 232 emu/g was obtained and the difference is less than 2% and relatively small.

Magnetic torque curves were measured under a range of external magnetic fields lower than 10 kOe, shown in Fig. 3. The torque curve under magnetic fields lower than the coercive field of 3.5 kOe showed almost two-fold symmetry (Fig. 3 (a)), which changed to four-fold symmetry as the magnetic field was increased (Fig. 3 (b)–(d)). The rotational hysteresis almost disappeared in the torque curve at 8.0 kOe, though the curve still deviated from a simple sinusoidal curve.

The torque curves for the aligned  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> NPs clearly show hysteresis loss at the middle range of the external magnetic field due to the hysteretic feature of magnetization curves, and they are plotted against the amplitude of the external field (Fig. 4). Peaks in the curves were found at around 4 kOe for both aligned and random samples. The hysteresis loss was plotted against the inverse of the magnetic field (Inset of Fig. 4). The anisotropy field ( $H_k$ ) was estimated from these plots using linear fits of straight lines,<sup>16</sup> as shown in the inset of Fig. 4. The estimated amplitude of  $H_k$  was 8.0 kOe for both samples. From the relationship  $K_u = M_s H_k / 2$  (using the Stoner-Wohlfarth (SW) model),  $K_u$  of  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> was calculated as 6.9 Merg/cm<sup>3</sup>. It should be noted that  $H_k$  did not vary with

TABLE I. Mossbauer parameters, hyperfine field ( $H_{hf}$ ), isomer shift (I.S.), quadrupole split (Q.S.), and area ratio for  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> aligned nanoparticles at 4.2 K.

Phase	Site	$H_{hf}$ (kOe)	I.S.(mm/s) <sup>a</sup>	Q.S. (mm/s)	Area (%)
Fe <sub>16</sub> N <sub>2</sub>	4e	304	0.200	−0.313	13.8
	8h	334	0.28	0.166	25.4
	4d	423	0.315	−0.162	15.2
Fe-O	D	−	0.448	1.97	11.6
	M	486	0.513	−0.05	34.0

<sup>a</sup>Relative to room temperature  $\alpha$ -Fe.

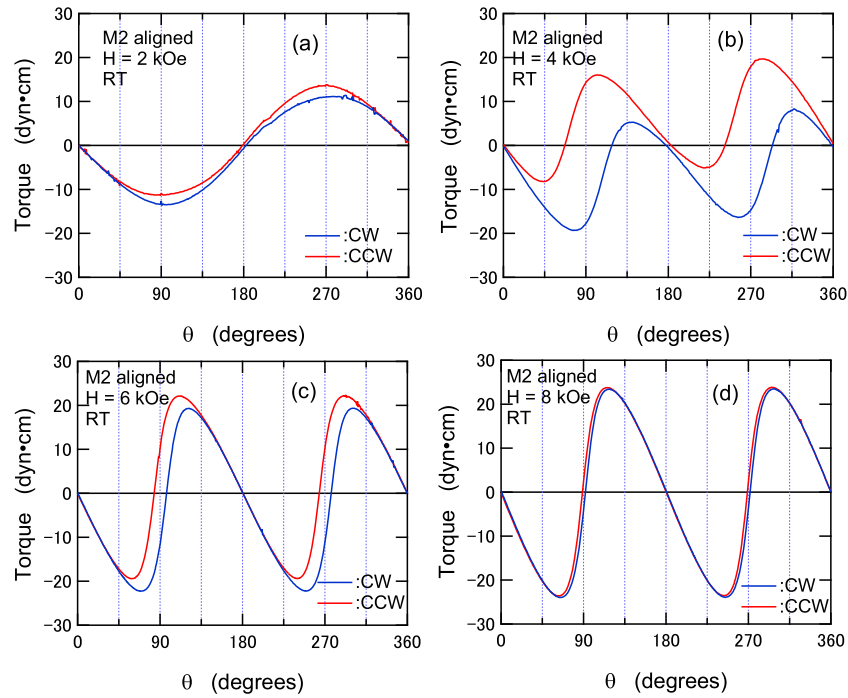


FIG. 3. Typical magnetic torque curves for the aligned  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> particles sample (M2) at an external field of (a) 2 kOe, (b) 4 kOe, (c) 6 kOe, and (d) 8 kOe. Rotational hysteresis was clearly observed in the curves below 6 kOe.

different degrees of alignment. The hysteresis loss has been studied using numerical simulation for the coherent rotation (SW) and the fanning models. For both aligned and random samples, the peak positions of the hysteresis loss against the external field did not change significantly, although the peak height remarkably decreased for the random samples.<sup>17</sup> The peak found in the present study was not sharp compared with the theoretically calculated one,<sup>13</sup> and distribution in magnetic anisotropy was suggested. The difference in peak height between the aligned and random samples qualitatively agreed with the theoretical simulation.

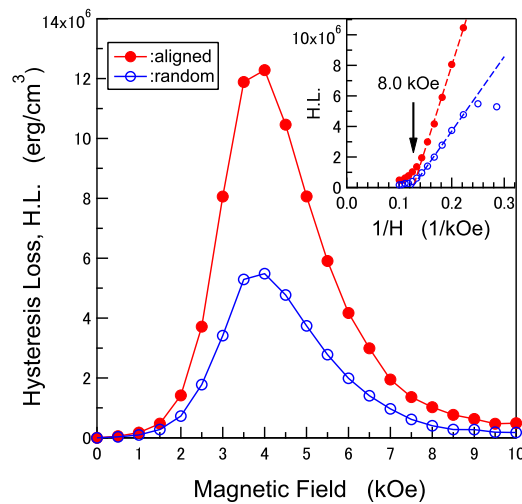


FIG. 4. Rotational magnetic hysteresis loss energy (H.L.) calculated from the torque measurements for  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> nanoparticles. Closed “red” circles and open “blue” circles show data for the magnetically aligned sample and the non-aligned (random) sample, respectively. In the Inset, the hysteresis losses were plotted against the inverse of the external magnetic field. The anisotropy field ( $H_k$ ) was found to be 8.0 kOe where the linear line intersects with the abscissa.

The magnetic anisotropy of  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> has been studied for various samples, including NPs<sup>10,12,13</sup> and thin films.<sup>7</sup> Ogawa reported the performance of sub-micron sized particles with a diameter of 0.2  $\mu$ m whose Mossbauer spectra indicate the particles are in a single-phase state;<sup>12</sup> the anisotropy energy amplitude from their study was reported as 9.6 Merg/cm<sup>3</sup>. From the size of the particles, the values is considered to be that for the bulk state. Our results were obtained using NPs with 20 nm diameters, much smaller than those used in the study of Ogawa.

The assignment of phases for magnetic subspectra in Mossbauer spectroscopy usually includes a 2-3% error due to insufficient statistics. The intrinsic uncertainty related to the recoil free ratio can be lowered by recording the spectrum at the lowest temperature, eliminating the influence of recoil absorption. The sample where the ratio of Fe atoms in  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> compared to the whole sample changes from 56.2 % at room temperature to 54.4% at 4.2 K shows a relatively small temperature dependence. The valence state of Fe atoms in the shell was mostly found to be 3+; however, the structure of shell Fe oxides was not well determined and might have a spinel-like structure with a small amount of Fe<sup>2+</sup> atoms. This leads to an uncertainty in the volume and weight of the oxides in the sample and a corresponding error in the calculation of the saturation magnetization as large as 2 %. Therefore, we estimated the maximum error to be 5 % in resulted magnetization and anisotropy.

Other techniques have been examined for the determination of phase concentration. X-ray and neutron diffraction have been used for bulk-like samples with high resolution achieved by the Rietveld refinement. An advantage of the latter<sup>18</sup> was pointed out in that there is less influence from penetration depth compared with the former technique. In the present case, the particle size is small and the presence of the amorphous phase was confirmed by TEM. In such cases, Mossbauer spectroscopy is meaningful in spite of the rather high estimated error of 5%.

In summary, the magnetic anisotropy energy for core-shell  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> NPs was evaluated by the rotational hysteresis loss measured from torque measurements. The saturation magnetization and anisotropy constant were evaluated to be 234 emu/cc and 6.9 Merg/cm<sup>3</sup>, respectively. These amplitudes coincide well with those for bulk-like single phase  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> particles. This crystalline anisotropy is still smaller than the shape anisotropy of the thin films ( $2\pi M_s^2 = 20$  Merg/cm<sup>3</sup>) and a perpendicular magnetic state is not expected for the thin film form. The characteristics is suitable for applications such as magnetic recording media<sup>9</sup> and bulk permanent magnets.<sup>13</sup>

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