Dynamic hysteresis measurement of magnetic nanoparticles with aligned easy axes

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Magnetic particle imaging (MPI) is a novel diagnostic imaging technique based on the use of magnetic nanoparticles (MNPs). Investigating the magnetic properties of magnetic nanoparticles is important for achieving a high spatial and temporal resolution in MPI. In this study, γ-Fe₂O₃ nanoparticles (core diameter: \(d_c = 4\) nm), Fe₃O₄ nanoparticles (\(d_c = 20–30\) nm), and Resovist® were immobilized in a DC magnetic field with their easy axes aligned. DC and AC magnetization curves were measured for the prepared MNPs. The measurements were performed by applying fields parallel and perpendicular to the easy axis and evaluating the magnetic properties of the MNPs for the easy and hard axes. The direction of magnetic moments under the AC magnetic field applied to the direction of the easy axis or hard axis was evaluated using both experimental results and numeric simulation using the Landau–Lifshitz–Gilbert equation to reveal magnetic relaxation property at wide frequency range and the effect of core size distribution of oriented MNPs. The effect of anisotropy in superparamagnetic nanoparticles, the relaxation property depending on the anisotropy energy barrier, and the fast magnetization process of Néel relaxation were successfully observed.

**Keywords:** magnetic nanoparticle, magnetic particle imaging, magnetic relaxation, magnetic easy axis, magnetization curve

1 Introduction

Magnetic nanoparticles (MNPs) are promising candidates for biomedical applications such as cancer treatment and diagnostic imaging\(^1\). In particular, magnetic nanoparticle imaging (MPI) is attracting attention owing to its potential for novel diagnostic applications\(^2\). MPI is an imaging technique that detects MNPs directly through the nonlinearity of their magnetization. In vivo cancer imaging using MPI has been reported with characteristic spatial resolution of approximately 1 mm\(^3\). The MPI signal is strongly dependent on the size or structure of the used particle\(^4\), so the resolution of MPI can be improved by optimizing these parameters. To achieve high spatial and temporal resolution of MPI, the magnetic properties of MNPs should be investigated, and optimal conditions related to the applied field and the MNP parameters should be determined. In this study, we fabricated samples from MNPs with aligned easy axes and measured their magnetic properties.

Orientation of the easy axes of MNPs in an AC field obtained by simulations and experiments has been reported previously\(^5\). The orientation of the easy axes should be considered in MPI, which uses an AC magnetic field for diagnosis. It is important to clarify the magnetic properties of MNPs in an AC field with regard to the degree of anisotropy. Magnetization measurement at 20 kHz and its harmonic signal of oriented MNPs have been reported by Yoshida et al.\(^6\). We measured magnetization curves for superparamagnetic and ferromagnetic iron-oxide nanoparticles with aligned easy axes under an AC magnetic field with a frequency up to 500 kHz considering their relaxation properties, and observed clear anisotropy of the MNPs in this study. As magnetic properties certainly depend on the core size of MNPs\(^4\), the effect of core size distribution was also studied with using the oriented MNPs.

The energy of an MNP placed in an external magnetic field consists of the anisotropy energy and the energy associated with the external magnetic field, as given by the Stoner–Wohlfarth model:

\[
E = K_v V_M \sin^2 \theta - \mu_0 M H \cos(\phi - \theta) \quad (1)
\]

where \(K_v\), \(V_M\), \(\theta\), \(\mu\), \(M\), \(H\), and \(\phi\) are the magnetic anisotropy constant, the volume of the primary particle, the angle between the easy axis and the magnetic field, the permeability of free space, the magnetization of the MNP, the intensity of the external field, and the angle between the easy axis and the magnetization, respectively\(^10\). Magnetic moments tend to align with the direction of the magnetic easy axis and the magnetic field to minimize the anisotropy energy and the energy associated with the external magnetic field, respectively. The anisotropy energy depends on the size of the MNP. In a superparamagnetic nanoparticle, the orientation of the magnetic moment is randomized by the thermal energy, and the magnetic properties show no coercivity or remanence because the anisotropy energy is smaller than the thermal energy.

When an AC field is applied to the MNP’s, magnetic relaxation occurs owing to the delay of magnetization in the AC field. Néel relaxation time \(\tau_N\) derived from the
rotation of the magnetic moment is given by the following equation:

$$\tau_N = \tau_0 \exp \left( \frac{K_V V_M}{k_B T} \right), \quad (2)$$

where \( \tau_0 \) is the attempt time, \( k_B \) is the Boltzmann constant, and \( T \) is the temperature, respectively.\(^{11,12}\)

### 2 Materials and methods

#### 2.1 Materials and samples

Water-dispersed \( \gamma \)-Fe\(_2\)O\(_3\) nanoparticles supplied from Meito Sangyo Co. Ltd. with core diameters (\( d \)) of 4 \( \text{nm} \) were used as superparamagnetic nanoparticles. They were coated with carboxymethyl-diethylaminoethyl dextran. In addition, Fe\(_3\)O\(_4\) nanoparticles purchased from Nanostructured and Amorphous Materials Inc. with \( d \) of 20–30 \( \text{nm} \) were used as ferromagnetic nanoparticles. They were coated with polyethyleneimine to achieve better dispersion in the solution.

Two types of solid samples were prepared for either type of MNPs. One solid sample contained MNPs fixed with epoxy bond in the absence of magnetic fields, and the other solid sample contained MNPs fixed in a DC magnetic field applied with an electromagnet for 8 h. Thus, the easy axes of MNPs in the first sample were oriented randomly. In contrast, in the second sample, the magnetic easy axes of the MNPs were aligned. The intensity of the DC field during the preparation of the sample with aligned easy axes was 575 kA/m. The concentration of MNPs in both types of samples was adjusted to 2 mg-Fe/ml.

We also prepared samples with the aligned easy axes using Resovist\(^\text{®}\), a contrast agent generally used in MRI. Resovist\(^\text{®}\) is a commercially available MNP that indicates superparamagnetic behavior\(^5\) and is generally used for experiments on MPI\(^2\) and hyperthermia\(^3\). It has been reported that Resovist\(^\text{®}\) consists of multi core particles with their certain size distribution. The magnetic property of Resovist\(^\text{®}\) was compared with those of the \( \gamma \)-Fe\(_2\)O\(_3\) (4 \( \text{nm} \)) samples which exhibited smaller core size distribution\(^5\).

#### 2.2 Magnetization measurements

DC magnetization curves were measured with a vibrating sample magnetometer (VSM), and AC magnetization curves were measured with a pickup coil at a frequency of 1–100 kHz under the amplitudes of the applied field of 4 kA/m and 16 kA/m\(^{10}\). For the solid sample with aligned easy axes, DC and AC hysteresis measurements were performed by applying magnetic fields parallel and perpendicular to the easy axis, which we defined as the easy axis sample and the hard axis sample, respectively. All measurements were taken at 298 K. The saturation magnetization of the sample was estimated by fitting the measured DC magnetization curve at the field intensity of 800 kA/m to calculate the magnetization curve from the Langevin function.

2.3 Numerical simulation

In the magnetization measurement, the results indicate the total magnetization of MNPs in the sample. Therefore, the magnetic states and magnetization distribution of individual MNPs were evaluated by numerical simulations. Numerical simulations were performed using the Landau–Lifshitz–Gilbert (LLG) equation\(^7,10\):

\[
\frac{dm}{dt} = -\gamma \left[ m \times \left( H + \alpha m \times H \right) \right], \quad (3)
\]

where \( m \), \( \gamma \), \( \alpha \), and \( H \) are the magnetization, gyromagnetic ratio, damping parameter (\( \alpha = 0.1 \)), and effective field, respectively. The magnetization was calculated as the value normalized by the saturated magnetization according to Eq. (3) using the Runge–Kutta algorithm. The gyromagnetic ratio is estimated by

\[
\gamma = \frac{\mu_0 M_{V_M}}{2 \alpha \tau_N k_B T}, \quad (4)
\]

where \( M_{V_M} \) is the saturated volume magnetization of 351 kA/m. The effective field is given by

\[
H = H_{ex} + H_{ani} + H_{th} \quad (5)
\]

In this equation,

\[
H_{ani} = \frac{K_{ani}}{\mu_0 M_s} n, \quad (6)
\]

where \( H_{ex}, H_{ani}, H_{th}, \) and \( n \) are the excited field, the magnetic anisotropy field, the fluctuating field due to thermal noise, and a unit vector along the easy axis, respectively. The thermal fluctuating field is satisfied by the following equations:

\[
\left\langle H_{th,i}(t) \right\rangle = 0 \quad (7)
\]

\[
\left\langle H_{th,i}(t)H_{th,j}(t') \right\rangle = \frac{2\alpha}{1 + \alpha^2} \frac{k_B T}{\mu_0 M_{V_M}} \delta(t - t') \left( \delta(t - t') \right). \quad (8)
\]

In these equations, \( i \) and \( j \) are Cartesian indices of different particles, \( \delta(\cdot) \) is the Kronecker delta function, and \( \delta \) is the Dirac delta function. The AC field of 16 kA/m at 100 kHz was applied parallel and perpendicular to the easy axis as in the experiments. In the numerical simulations, 28,672 particles were set with core diameters of 5±2 nm (mean±SD) and magnetic anisotropy constants of 20±1 kJ/m\(^3\), which followed the Gaussian distribution. There was no relation between the core diameters and the magnetic anisotropy constants. The easy axes of MNPs were completely oriented to same direction. Distributions of the number of particles were evaluated according to their dependence on the orientation of magnetization.

### 3 Results and discussion

#### 3.1 DC magnetization curves

Figure 1 and Figure 2 show the DC magnetization curves of both samples at field intensities of 800 kA/m and 4 kA/m, respectively. The magnetization was
normalized by saturation magnetization and represented in the unit of $M/M_s$. At the intensity of 575 kA/m, which corresponds to the intensity of the DC field during the preparation of the sample with aligned easy axes, magnetization greater than 85% of the saturation magnetization is observed in the sample with randomly oriented MNPs. For $\gamma$-Fe$_2$O$_3$ (4 nm) nanoparticles (Fig. 2 (a)), the coercivity of the DC magnetization curves in all samples is marginal. This is because the anisotropy energy is smaller than the thermal scattering energy at 298 K owing to the small volume of the measured $\gamma$-Fe$_2$O$_3$ (4 nm) nanoparticles. Therefore, the magnetic moments are randomly oriented, and the total magnetization at zero field is zero, which is characteristic of superparamagnetic nanoparticles. The magnetizations in the easy axis sample and hard axis sample were larger and smaller than that in the random sample, respectively. Clear anisotropy of the superparamagnetic nanoparticles at 298 K is observed. The distribution of the magnetic moments is shown in Fig. 3. When the magnetic field is applied to the MNPs, the magnetic moments tend to align with the easy axis owing to the energy associated with the applied field, and then the easy axis and the hard axis indicate the directions of large and small magnetization, respectively. In the absence of the magnetic field, the magnetic moments tend to align with the easy axis, but because they are randomly oriented owing to the thermal energy, the total magnetization is zero at zero field.

On the other hand, Fe$_3$O$_4$ (20–30 nm) nanoparticles exhibit large magnetization and coercivity when the magnetic field is applied parallel to the easy axis and small magnetization and coercivity when the magnetic field is applied along the hard axis, as shown in Fig. 2 (b). This is because the anisotropy energy barrier is large for the easy axis sample and small for the hard axis sample.

3.2 AC magnetization curves

Figure 4 and Figure 5 show the DC magnetization curves and AC magnetization curves of Fe$_3$O$_4$ (20–30 nm) nanoparticles at field frequencies of 1–100 kHz and intensities of 4 kA/m and 16 kA/m, respectively. The coercivities of the DC and AC magnetization curves are very similar at the field intensity of 4 kA/m regardless of the easy axis direction. It can be concluded that the magnetic moment does not exhibit detectable rotation at such small field intensities as 4 kA/m owing to the large diameters of the particles. In contrast, at large field intensities such as 16 kA/m, the coercivities of the DC and AC magnetization curves are very similar for the field applied along the hard axis. However, the coercivity of the DC magnetization curve is smaller.

![Fig. 1 DC magnetization curves of (a) $\gamma$-Fe$_2$O$_3$ (4 nm) and (b) Fe$_3$O$_4$ (20–30 nm) at field intensity of 800 kA/m.](image1)

![Fig. 2 DC magnetization curves of (a) $\gamma$-Fe$_2$O$_3$ (4 nm) and (b) Fe$_3$O$_4$ (20–30 nm) at field intensity of 16 kA/m.](image2)
than that of the AC magnetization curve for the field applied along the easy axis. We can conclude that magnetization reversal occurs at 16 kA/m. The coercivity remains constant for the frequency range of 1–100 kHz. This is because the peak frequency of Néel relaxation for the Fe₃O₄ (20–30 nm) nanoparticles calculated from Equation (2) is less than 0.01 Hz ($K_u = 23$ kJ/m³)¹⁷ and lies almost outside of the measured frequency range.

Figure 6 shows a comparison between the AC magnetization curves for the samples of Fe₃O₄ nanoparticles with easy axis sample, hard axis sample, and random sample at a frequency of 10 kHz and intensity of 16 kA/m. As the DC magnetization, the easy axis sample shows the highest value, whereas the hard axis sample shows the lowest. The harmonic signal in MPI can be increased by applying an AC field along the easy axis due to larger magnetization of the MNP. Although the coercivities of the DC magnetization curves are marginal in all samples, the easy axis sample shows the highest coercivity, whereas the hard axis sample shows the lowest. This behavior indicates that there is a delay between the magnetization and the applied field associated with the angle between the applied field and the easy axis, which implies a difference in the anisotropy energy barrier. Similar results for superparamagnetic nanoparticles and ferromagnetic nanoparticles have been obtained previously from both numerical simulations and experiments.¹⁸–₂⁰

Figure 7 shows the distribution of the number of particles for the 5±2 nm particles obtained from numerical simulations at a frequency of 100 kHz and intensity of 16 kA/m. The horizontal and vertical axes indicate the magnetization of MNP and the percentage distribution of particles, respectively. The maximum value of the distribution, which describes the percentage of particles with reversed magnetization, is

![Figure 3](image-url)

**Fig. 3** Distribution of magnetic moments when magnetic field is applied to (a) easy axis and (b) hard axis. Distribution of magnetic moments at zero field (c).

![Figure 4](image-url)

**Fig. 4** DC and AC magnetization curves of Fe₃O₄ (20–30 nm) nanoparticles at field intensity of 4 kA/m. Direction of applied field was along (a) easy axis and (b) hard axis.

![Figure 5](image-url)

**Fig. 5** DC and AC magnetization curves of Fe₃O₄ (20–30 nm) nanoparticles at field intensity of 16 kA/m. Direction of applied field was along (a) easy axis and (b) hard axis.
Fig. 6 AC magnetization curves of γ-Fe₂O₃ (4 nm) nanoparticles at frequency of 10 kHz. Intensity of field was 16 kA/m.

greater in the easy axis sample than in the randomly oriented sample. However, there are some particles whose magnetization is opposite to the applied field in the easy axis sample owing to the strong binding force associated with the large anisotropy energy barrier. In the hard axis sample, the maximal value of the distribution is observed at approximately ±0.2 M/Mₘ. This indicates that the magnetic moments are predominantly aligned along the easy axis rather than magnetization reversal.

The DC and AC magnetization curves of the γ-Fe₂O₃ (4 nm) nanoparticles at frequencies of 1–100 kHz and intensity of 16 kA/m are shown in Fig. 8. In Fig. 8 (a), the coercivity of the easy axis sample clearly increases with increasing frequency. In contrast, the coercivity of the hard axis sample is marginal up to 100 kHz, as shown in Fig. 8 (b). According to the results of numerical simulations (Fig. 7), magnetic relaxation occurs with a large delay relative to the applied AC magnetic field in the easy axis sample. In contrast, magnetic reversal does not occur in the AC field with the oscillation of the magnetic moment on the easy axis in the hard axis sample. Thus, hysteresis is not observed in the magnetization curves of the hard axis sample even at high frequencies. This manifests an experimental observation of the fast Néel relaxation process.

The magnetization (M/Mₘ) under the applied field of 16 kA/m during the magnetization reversal at 100 kHz was calculated by summation of distributed magnetization shown in Fig. 7. The magnetizations of random, easy axis, and hard axis samples were derived as 0.21, 0.30, and 0.11 M/Mₘ from Figs. 7(a), (b), and (c), respectively. The calculated values of magnetizations of easy axis and hard axis samples were compared with the measured magnetization shown in Fig. 8. As indicated by the arrows in the figure, the measured magnetization under the applied field of 16 kA/m at 100 kHz were 0.25 and 0.20 M/Mₘ for the easy axis and hard axis samples, respectively. The difference between 0.25 and 0.20 M/Mₘ is smaller than that between calculated values of 0.30 and 0.11 M/Mₘ, which can be explained by imperfection of particle orientation in the prepared samples. In spite of this quantitative analysis, the simulated magnetization agreed well qualitatively with the measured AC magnetization curves in terms of characterization of difference in the easy axis and hard axis samples.

Figure 9 compares the AC magnetization curves of
the γ-Fe₂O₃ (4 nm) nanoparticles with those of Resovist®, measured at a frequency of 500 kHz, the core size distribution of Resovist® has been reported [1]. These particles of large diameters with longer Néel relaxation time than that of γ-Fe₂O₃ (4 nm) exhibit large coercivity in both the easy axis and hard axis samples.

4 Conclusions

In this study, samples of immobilized particles of γ-Fe₂O₃ (d = 4 nm), Fe₃O₄ (d = 20–30 nm), and Resovist®, whose easy axes were aligned or randomly oriented, were prepared. Their DC and AC magnetization properties up to 500 kHz were analyzed, and the effect of easy axis orientation on superparamagnetic nanoparticles and ferromagnetic nanoparticles was evaluated. In both superparamagnetic γ-Fe₂O₃ (d = 4 nm) and ferromagnetic Fe₃O₄ (d = 20–30 nm) nanoparticles, the DC and AC magnetization curves indicated larger and smaller magnetization due to anisotropy energy, when the field was applied to the easy axis and hard axis of the samples, respectively. The increase of magnetization under an applied AC field along the easy axis is expected to increase the harmonic signal in MPI. In the case of γ-Fe₂O₃ (4 nm) nanoparticles, the superparamagnetic feature was clearly observed with random orientation of the easy axis, regardless of the alignment of immobilized particles. In the AC magnetization curves of the γ-Fe₂O₃ (4 nm) nanoparticles, there was an increase in coercivity with increasing field frequency applied to the easy axis direction. In contrast, when the field was applied to the hard axis, the coercivity was almost marginal up to 100 kHz so that magnetization could follow the applied magnetic field even at high frequency. Thus, the fast magnetization process of Néel relaxation was experimentally observed. The AC magnetization curve of Resovist®, measured at a frequency of 500 kHz, indicated larger coercivity than that of the γ-Fe₂O₃ (4 nm) nanoparticles. This is because Resovist® has a longer Néel relaxation time owing to the larger core size of the particles compared to γ-Fe₂O₃ (4 nm). The frequency characteristics and effect of core size distribution of MNPs both in the easy axis and hard axis were prepared. Their DC and AC magnetization curves of γ-Fe₂O₃ (4 nm) at frequencies of 1–100 kHz and intensity of 16 kA/m with model of magnetic moment distribution. Direction of applied field was along (a) easy axis and (b) hard axis.

Fig. 8 DC and AC magnetization curves of γ-Fe₂O₃ (4 nm) at frequencies of 1–100 kHz and intensity of 16 kA/m with model of magnetic moment distribution. Direction of applied field was along (a) easy axis and (b) hard axis.

Fig. 9 AC magnetization curves of γ-Fe₂O₃ (4 nm) nanoparticles and Resovist® at field intensity of 4 kA/m and frequency of 500 kHz. Direction of applied field was along (a) easy axis and (b) hard axis.
directions were clearly revealed.

In addition, numeric simulation using the LLG equation was performed to understand magnetization distribution of individual MNPs, and the results agreed well qualitatively with the experimental results. The calculated results successfully demonstrated that a large proportion of magnetization was reversed by the application of an AC field to the easy axis and that there remained particles whose magnetization direction was opposite to the applied field owing to the strong binding force associated with the large anisotropy energy barrier. When the AC field was applied to the hard axis, the magnetization, which was predominantly aligned to the easy axis, was oscillated by the applied field.

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