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THERMAL FLUCTUATION AND MAGNETIZATION OF Ni–Zn FERRITE NANOPARTICLES BY PARTICLE SIZE

Y. Ichiyanagi[1*], *T. Uehashi*[1], *S. Yamada*[1], *Y. Kanazawa*[2] *and T. Yamada*[2]

[1]Department of Physics, Graduate School of Engineering, Yokohama National University, 79-5 Tokiwadai, Hodogaya, Yokohama 240-8501, Japan
[2]Department of Physics, Faculty of Engineering, 79-5 Tokiwadai, Hodogaya, Yokohama 240-8501, Japan

$Ni_{1-x}Zn_xFe_2O_4$ ($0 \le x \le 1$) mixed ferrite nanoparticles encapsulated with amorphous-SiO_2 were prepared by a wet chemical method. Particle sizes were controlled to range from 2.6 to 33.7 nm by heat treatment, and the particle size dependence of saturation magnetization M_s was investigated for the x=0.5 region. The M_s value decreased abruptly for particle sizes below about 6 nm. From the temperature dependence of the magnetization under field-cooled and zero-field-cooled conditions, blocking temperatures T_b were observed to be between 28 and 245 K depending on the particle size. At the blocking temperature, the superparamagnetic spins in the particle are supposed to be blocked against the thermal fluctuation energy. A smaller particle volume causes a lower blocking temperature; so an extremely small particle would be strongly affected by thermal fluctuation.

Keywords: *magnetization, nanoparticle, Ni–Zn ferrite, thermal fluctuation*

Introduction

Magnetism of nanoscopic systems has drawn much attention due to the unique magnetic properties as well as the technological applications of such systems. The authors have reported magnetic properties of $Ni(OH)_2$ nanoclusters [1–5], Fe-oxide nanoclusters, Fe–Co–O nanoscopic systems [6], Co-oxide nanoparticles [7], NiO nanoparticles [8], and Ni–Zn ferrite nanoparticles. $Ni(OH)_2$ nanoclusters were revealed as monolayer hexagonal structures with a ferromagnetic transition temperature of T_C~10 K, while bulk crystal is antiferromagnetic with a Néel temperature of T_N=25.75 [9]. A large coercivity of about 1 kOe, even at 300 K, was observed in the Fe–O nanoparticles because of the coexistence of the γ-Fe_2O_3 and α-Fe_2O_3 phases [10]. NiO and Co_3O_4 bulk crystals exhibit Néel temperatures of 523 and 33 K, respectively; however, the Néel temperatures could not be observed and ferromagnetic behavior with hysteresis was found below 10 K. Some reports have suggested that NiO should exhibit weak ferromagnetism or superparamagnetism for fine particles. These ferromagnetic behaviors at low temperature regions might be explained by uncompensated surface spins of antiferromagnetic fine particles. For Co doped Fe_2O_3 nanoparticles the largest coercivity was observed near a Co/Fe mole ratio of 0.4, where $CoFe_2O_4$ (Co-ferrite) particles might be newly produced [10]. Transition metal ferrites and transition metal alloys exhibit interesting phenomena also in thermal measurements [11, 12].

It is an interesting phenomenon that when adding Zn ions to spinel ferrites, their magnetization increases according to the Zn content, even though Zn ions are non-magnetic [13]. The authors have reported that this tendency could be observed up to a Zn content value (x) of about 0.5 or 0.6 in a formula unit of $Ni_{1-x}Zn_xFe_2O_4$ nanoparticles with diameters of about 6 nm [14]. However, the absolute values of saturation magnetization M_s in the nanoparticles were about 30% smaller than those of bulk crystal. This phenomenon could be explained by the canting of surface spins of small particles at definite angle [15], or the ion distribution [16]. In this report Zn content was fixed at x=0.5, the particle sizes were controlled by the annealing temperature and time; after which the particle size dependence of magnetization was investigated.

Ni–Zn nanoparticles were produced and particles sizes controlled between 2.5 and 33.7 nm. Nanoparticles with such particle sizes usually form a single domain. Magnetic spins in a domain are ferromagnetically coupled and are fluctuated by thermal energy above the blocking temperature T_b. In this work, the relationship between magnetization and thermal fluctuation in a nanoscopic system was investigated in detail.

* Author for correspondence: h042301d@mbox.nagoya-u.ac.jp

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

Experimental

$Ni_{1-x}Zn_xFe_2O_4$ ($0 \leq x \leq 1$) mixed ferrite nanoparticles encapsulated by a host network of SiO_2 were prepared by a wet chemical method. Aqueous solutions of nickel chloride ($NiCl_2 \cdot 6H_2O$), zinc chloride ($ZnCl_2$), iron chloride ($FeCl_2 \cdot 4H_2O$) and sodium metasilicate nonahydrate ($Na_2SiO_3 \cdot 9H_2O$) were each mixed and stirred to obtain their respective precipitates, which were washed several times with distilled water and dried at about 350 K in a water bath. The solids obtained were calcined between 873 and 1373 K.

The prepared samples were examined by X-ray powder diffraction and chemical analysis, and then magnetization measurements were performed with a VSM and SQUID magnetometer under an external field between –50 and 50 kOe at a temperature range from 5 to 300 K.

Differential thermal analysis and thermogravimetric (DTA-TG) measurements were carried out with an ULVAC 700-RH in air. The measured temperature region was between room temperature and 1073 K.

Results and discussion

X-ray analysis

The X-ray powder diffraction patterns of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ annealed at six different temperatures are shown in Fig. 1. The mole ratio of the contents of this sample was Ni:Zn:Fe:Si=1:1:4:7 by chemical analysis (icp). In all cases the spinel phase with a lattice constant of about 0.840 nm could be produced, even though the patterns for the samples annealed at lower temperatures are fairly broad because of large amounts of amorphous SiO_2. The particle size of the spinel phase was estimated from the broadening of the diffraction peaks using the Scherrer formula. The diameters of the obtained particles ranged between 2.6

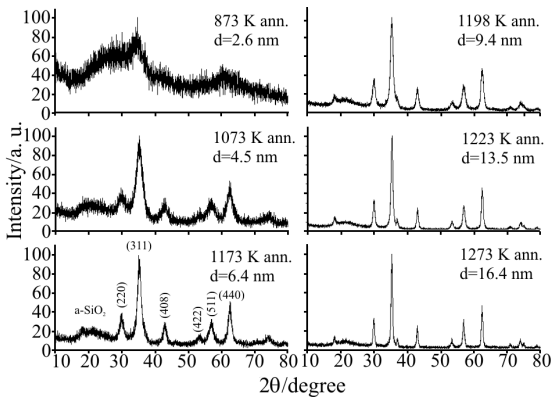

Fig. 1 Powder X-ray diffraction patterns of the sample of being annealed at various temperatures for 10 h

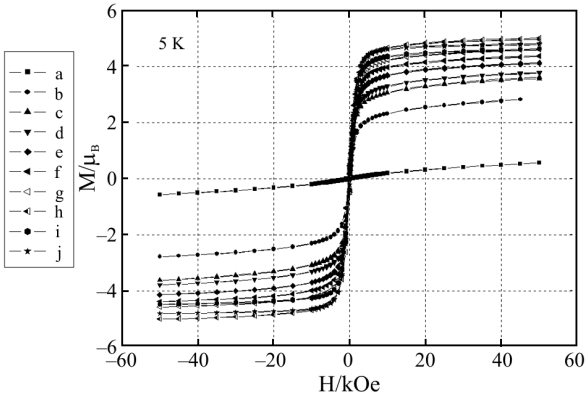

Fig. 2 The *M-H* curves for each particle size. The letters a, b, c, d, e, f, g, h, i and j in the figure correspond to particle sizes of 2.6, 4.5, 6.4, 9.4, 13.5, 16.4, 20, 25, 29.7 and 33.7 nm, respectively

and 33.7 nm, depending on the annealing temperature and the time. Particle size increased as the annealing temperature as well as the annealing time increased; thus, it is possible to control grain size by the annealing temperature and time.

Annealing temperature was controlled between 873 and 1373 K, and time between 10 and 25 h. Particle sizes obtained were 2.6, 4.5, 6.4, 9.4, 13.5, 16.4, 20, 25, 29.7 and 33.7 nm, respectively.

TG-DTA measurement

In order to clarify the transformation process, differential thermal analysis and thermogravimetric (DTA-TG) measurements were carried out by ULVAC 700-RH under air circumstances. In the TG curve, the mass loss by dehydration was observed above 370 K, and then the sample mass gradually decreased at higher temperature up to 773 K. From the DTA curve endothermic peak was observed at around 380 K, corresponding to the above hydration, however, no remarkable change was observed up to 773 K, though a strong exothermic effect for $Ni_{0.65}Zn_{0.35}Fe_2O_4$ ferrite powder was reported [17].

Magnetization curves

Magnetization measurements were performed for all samples of $Ni_{0.5}Zn_{0.5}Fe_2O_4$. The region of the measured temperatures was between 5 and 300 K, and the external field was ±50 kOe.

The *M–H* curves for each particle size are shown in Fig. 2. The letters a, b, c, d, e, f, g, h, i and j in the figure correspond to particle sizes of 2.6, 4.5, 6.4, 9.4, 13.5, 16.4, 20, 25, 29.7 and 33.7 nm, respectively. From this figure, it is obvious that the magnetization increases as the particle size increases. The magnitude of M_s of (a), namely a sample of 2.6 nm, was ex-

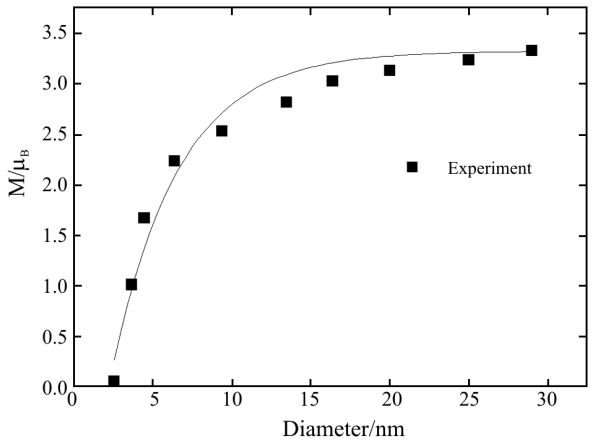

Fig. 3 The particle size dependence of saturation magnetization M_s

tremely small, however, coercivity was the largest with H_c=1110 Oe.

The value of saturation magnetization M_s was obtained by using higher fields and lower temperatures, and was extrapolated towards H=∞ and T=5 K. The particle size dependence of saturation magnetization is shown in Fig. 3; as particle size decreases, magnetization decreases gradually and abruptly changes at about 6 nm. The particle size dependence of the coercive force H_c is shown in Fig. 4; H_c increases drastically below 6 nm.

Figure 5 shows the temperature dependence of both field-cooled (FC) and zero-field-cooled (ZFC) magnetization for various particle sizes, under a 100 Oe field. If we define the bifurcated temperature of FC and ZFC as the blocking temperature T_b, T_b is found to be 28 K for d=2.6 nm, 61 K for d=4.5 nm, 138 K for d=6.4 nm and 245 K for d=9.4 nm, respectively. Above d=13.5 nm T_b could not be determined because it might be above 300 K. In a small particle below d=9.4 nm ferrimagnetic property of Ni–Zn ferrite bulk crystal could not be observed but transition

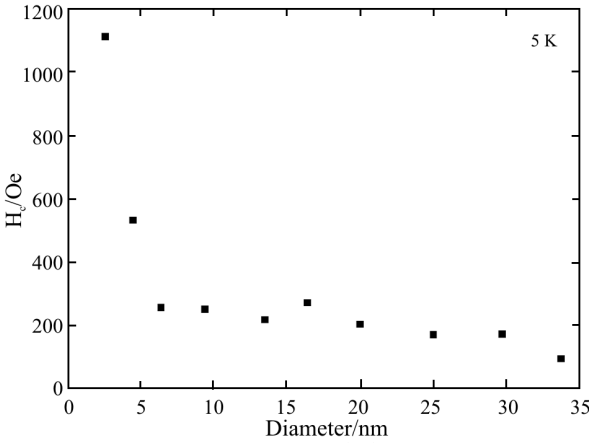

Fig. 4 The particle dependence size of the coercive force H_c

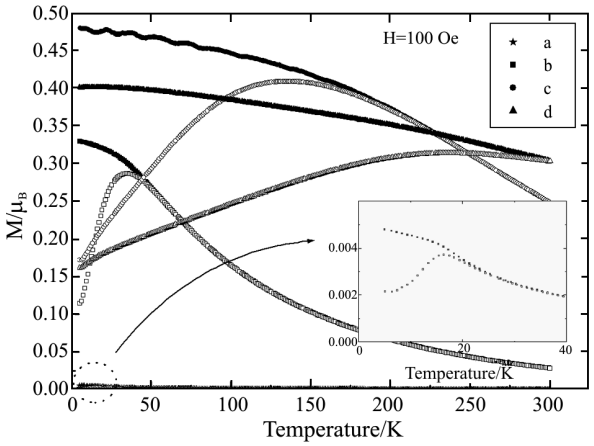

Fig. 5 Temperature dependence of both field-cooled (FC) and zero-field-cooled (ZFC) magnetization for various particle sizes, under a 100 Oe field

temperature was found far below T_C as T_b instead and ferromagnetic property below T_b was newly exhibited. Above the blocking temperature T_b, the magnetic spins in the particle are supposed to fluctuate with thermal energy and behave paramagnetically.

Thermal fluctuation

If we define the uniaxial anisotropy constant in a single domain as K_u, the volume of the particle as ν, and the angle between the magnetization and the magnetic easy axis as θ, anisotropy energy is displayed as

$$E = \nu K_u \sin^2 \theta \qquad (1)$$

This energy has a potential barrier at π/2 when the external field is applied in the π direction from the θ=0 position. In the case $\nu M_s H > \nu K$, magnetic spin can overcome the potential barrier and reverse the direction. If the volume of the particle is extremely small and $K_u\nu$ becomes smaller than thermal energy kT, magnetic spin easily reverses by thermal energy. As a result, a small particle behaves superparamagnetically, similar to paramagnetically, though the magnetic spins in a particle are ferromagnetically coupled.

The law of approach to saturation magnetization

If the magnetization is almost saturated by the external field, the saturation magnetization can be expressed by following equation,

$$M = M_s(1 - \frac{a}{H} - \frac{b}{H^2} - \cdots) + \chi_0 H \qquad (2)$$

In order to obtain it experimentally, (2) can be displayed as,

$$\frac{dM}{dH} = M_s(\frac{a}{H^2} + \frac{2b}{H^3} + \cdots) + \chi_0 \qquad (3)$$

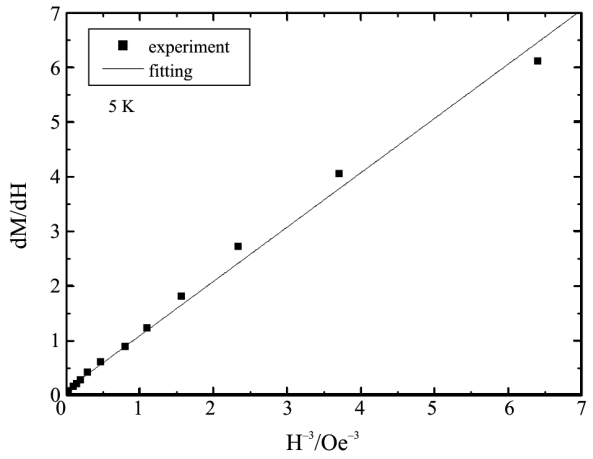

Fig. 6 The fitting resulting from the law of approach to saturation magnetization

where b is calculated as $8/105 \cdot K_1^2/M_s^2$.

If the experimental data follows linearly when plotted on dM/dH *vs.* $1/H^3$, we can estimate the b value from the gradient of the line and obtain the anisotropy constant K_1 [18, 19].

The fitting resulting from the law of approach to saturation magnetization is shown in Fig. 6.

From this result, the anisotropy constant K_1 was obtained as $|K_1|=2.88 \cdot 10^4$(J m^{-3}) at 5 K, and Ni–Zn ferrite bulk crystal as $|K_1|=15 \cdot 10^3$ (J m^{-3}) at 90 K. From this anisotropy constant, the blocking temperature T_b can be roughly estimated as T_b=68.5 K for the 5 nm size. T_b calculated in this way was higher than observed, which might be due to the thermal fluctuation being strongly influenced by a surface effect.

Conclusions

$Ni_{1-x}Zn_xFe_2O_4$ ($0 \leq x \leq 1$) mixed ferrite nanoparticles encapsulated with amorphous-SiO_2 were prepared by a wet chemical method. Particle sizes were controlled to range from 2.6 to 33.7 nm by heat treatment, and the particle size dependence of saturation magnetization M_s was investigated for the x=0.5 region. The M_s value decreased exponentially for particle sizes below about 6 nm. From the temperature dependence of the magnetization under field-cooled and zero-field-cooled conditions, blocking temperatures T_b were observed to be between 28 and 245 K depending on the particle size. At the blocking temperature, the superparamagnetic spins in the particle are supposed to be blocked against the thermal fluctuation energy. According to the law of approach to saturation magnetization, anisotropy constant was obtained. From this anisotropy constant, higher blocking temperature T_b was estimated. A smaller particle volume of causes a lower blocking temperature, so an extremely small particle would be strongly affected by thermal fluctuation.

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