Magnetic properties of NiO nanoparticles

Yuko Ichiyanagi [a,1], Naoto Wakabayashi [a] Junichiro Yamazaki [a] Saori Yamada [a] Yoshihide Kimishima [a], Eriko Komatsu [b], Hiroyuki Tajima [b]

[a] *Department of Physics, Yokohama National University, 240-8501 Yokohama, Japan*
[b] *ISSP, University of Tokyo, 277-8581, Kashiwa, Japan*

Abstract

NiO nanoparticles were produced by annealing $Ni(OH)_2$ monolayer-nanoclusters above 973 K in air. Their diameters were estimated to be between 2 and 6 nm from X-ray diffraction patterns. In the magnetization measurements superparamagnetic or ferromagnetic behaviours were observed and characteristic properties of NiO nanoparticles were confirmed.

Key words: nanoscopic systems; magnetization; Ni-oxide; magnetic clusters

1. Introduction

Magnetism of nanoscopic systems draws much attention due to their unique magnetic properties as well as their technological applications. The authors have reported magnetic properties of $Ni(OH)_2$ nanoclusters[1] and Fe-Oxide nanoclusters[2]. Each $Ni(OH)_2$ nanocluster was revealed as a monolayer hexagonal structure with the ferromagnetic transition temperature of $Tc \sim$10 K while bulk crystal of $Ni(OH)_2$ is antiferromagnetic with T_N of 24.8 K[1]. Larger coercivity of about 1 kOe, even at 300 K, was observed in the Fe-O nanoparticles because of the coexistence of $\gamma-Fe_2O_3$ and $\alpha-Fe_2O_3$ phases. In this study, an experimental investigation of NiO nanoparticles surrounded by amorphous SiO_2 with the average size ranging from 2.0 to 5.4 nm was performed. It is known that bulk crystal of NiO exhibits antiferromagnetism with T_N of 523 K. However, some reports suggested that NiO should exhibit weak ferromagnetism or superparamagnetism for fine particles[3][4]. In the present system, ferromagnetic behavior with slight hysteresis at 5 K, and superparamagnetic behavior above 30 K were observed.

[1] Corresponding author. E-mail: yuko@ynu.ac.jp

2. Experiment

The $Ni(OH)_2$ surrounded by amorphous SiO_2 precursors were produced by mixing aqueous solutions of $NiCl_2{\cdot}6H_2O$ and $Na_2SiO_3{\cdot}9H_2O$ at room temperature. They were washed with distilled water and dried at about 350 K. The resulting glassy bulk solids were pestled in a mortar for pulverization. The NiO nanoparticles were prepared by annealing chemically precipitated $Ni(OH)_2$ [1] in air for 10 hours at various temperatures between 773 K and 1373 K. X-ray diffraction patterns were obtained at room temperature using CuK_α radiation. Magnetization measurements were performed for each sample by a SQUID magnetometer under a magnetic field between -50 kOe and 50 kOe, and the temperature region from 5 K to 300 K.

3. Results and Discussion

NiO nanoparticles with diameters larger than 5.3 nm were obtained by annealing $Ni(OH)_2$ above 773 K. From the X-ray diffraction patterns, NiO particles surrounded by amorphous SiO_2 were confirmed for the samples annealed at temperatures between 973

K and 1073 K. Magnetization curves and saturation magnetizations also supported this result. Various annealing temperatures and obtained average diameters of nanoparticles are summarized in Table.1. Expected phases are also indicated.

sample No.	annealing temp.(K)	phase	d(nm)
0	as prepared	$Ni(OH)_2$	2.0
1	773	$Ni(OH)_2$	2.1
2	873	$Ni(OH)_2$	2.1
3	973	$Ni(OH)_2$+NiO	2.1
4	1073	NiO	3.0
5	1173	NiO	3.1
6	1273	NiO	5.4
7	1373	Ni_2SiO_4	37.8

Table 1
Particle size of NiO or $Ni(OH)_2$ nanoparticles depending on various annealing temperatures estimated from X-ray diffractions.

The single NiO phase was obtained without any observable traces of $Ni(OH)_2$ by X-ray diffractions for No.4,5 and 6 samples. The No.7 sample which was annealed at 1273 K exhibited Ni_2SiO_4 of bulk crystal. Magnetization measurements for all the samples were performed. Fig.1(a) shows $M - H$ curves for samples from No.3 to No.5 at 5 K when applying a magnetic field of ±50 kOe. No.4 and No.5 samples showed ferromagnetic behavior with slight hysteresis loops and coersivities of about H_C=750 Oe. Fig.1(b) shows mag-

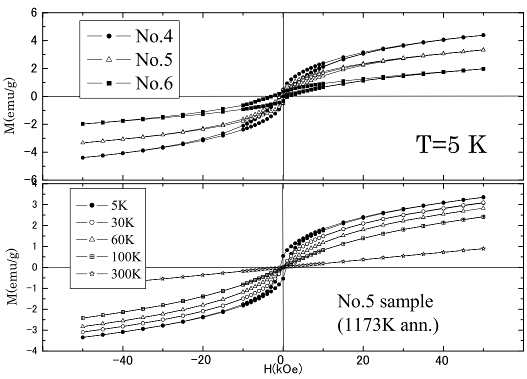

Fig. 1. (a)(upper)Magnetization curve at 5 K for the indicated sample numbers of nanoparticles corresponding to the Table.1. (b)(lower)Magnetization curve at 5 K, 30 K, 60 K, 100 K and 300 K for the No.5 sample, namely, annealed at 1173 K.

netizations measured at 5 K, 30 K, 60 K, 100 K and 300 K for the No.5 sample. Both magnetization increase with decreasing temperature for all temperature regions, and superparamagnetic behavior between the temperature of 30 K and 100 K, were observed. However, the curves do not fit the Brillouin function. These behaviors in spite of enough lower temperature below T_N=523K should be due to the uncompensated surface spins, particularly for extremely small particles with diameters of several nanometers. Considering the diameter of 3.1 nm and the lattice constant a=0.148 nm, the numbers of the surface spins can be roughly estimated as 172 spins. These surface spins may yield such ferromagnetic behaviors. Fig. 2 shows Field-Cooled and

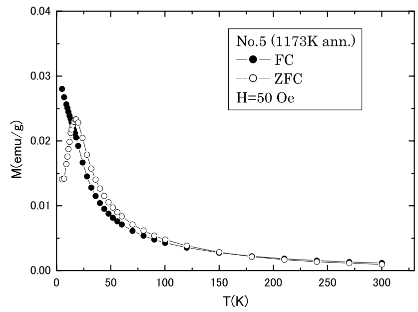

Fig. 2. Magnetization the No.5 sample for ZFC and FC in 50 Oe applied field as a function of temperature.

Zero-Field-Cooled magnetizations under the applying field of 50 Oe as functions of temperature for the No.5 sample. The peak in the ZFC curve at 20 K can be defined as the average blocking temperature T_B of the magnetic moments. It could be considered that above T_B, thermal energy became larger than the anisotropy energy of Ni^{2+} moments, so the magnetization of NiO nanoparticles showed superparamagnetic behavior.

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