Effects of Pressure on Magnetic Properties of Ferrihydrite Antiferromagnetic Nanoparticles

Y Komorida¹, N J O Silva², M Mito¹, H Deguchi¹, S Takagi¹, F Palacio² and V S Amaral³

¹ Faculty of Engineering, Kyushu Institute of Technology, Kitakyushu, 804-8550, Japan
² Instituto de Ciencia de Materiales de Aragón, CSIC-Universidad de Zaragoza, Zaragoza, 50009, Spain
³ Departamento de Física and CICECO, Universidade de Aveiro, Aveiro, 3810-193, Portugal

E-mail: g586402y@tobata.isc.kyutech.ac.jp

Abstract. The effects of pressure on iron oxide hydroxide ferrihydrite (FeOOH•nH₂O) nanoparticles with particle size of 4.7 ± 0.2 nm were investigated through DC magnetic measurements in the pressure region up to \( P = 13.5 \) kbar. The magnetization curve up to 50 kOe exhibits the coexistence of saturation and linear contributions. The value of high field susceptibility, the latter contribution, increases with increasing pressure for \( P \leq 10.0 \) kbar. In contrast, the former contribution, associated to the uncompensated moment, decreases for \( P \leq 10.0 \) kbar. At further pressure, there is no distinct pressure response. These effects of pressure are probably related to changes in the anisotropy energy due to the volume shrinkage.

1. Introduction
Magnetic nanoparticles have been the subject of growing interest in recent years from both scientific and theoretical points of view [1]. The ratio of surface area against particle volume increases as the particle size decreases, resulting in the occurrence of varied magnetic properties. Generally the magnetic nanoparticles are divided into three types, such as ferromagnetic, ferrimagnetic and antiferromagnetic ones, accordingly to the magnetic properties of their bulk counterparts.

In the ferrimagnetic \( \gamma \)-Fe₂O₃ (maghemite) nanoparticles with the diameter \( D \) of 6.5 nm, the effects of pressure on magnetic properties have been investigated [2]. The ferrimagnetic nanoparticles consist of a superparamagnetic core and a disordered surface. The magnetic properties of the maghemite nanoparticles depend on pressure; the magnetic moment of the core decreased with increasing pressure in the low-pressure region \( (P \leq 3.7 \) kbar\), and recovered at \( P \geq 3.7 \) kbar. This was interpreted as a pressure-induced down-and-up fluctuation of the number of \( \text{Fe}^{3+} \) ions constituting the core.

In the case of the antiferromagnetic nanoparticles, the intrinsic magnetization arises from uncompensated (canted) spins. These spins can be uniformly distributed on the surface, randomly distributed on surface, or randomly distributed over the particle. In the case of ferrihydrite, we found that the anisotropy energy barriers are randomly distributed over the particle, possibly associated to an in-particle random distribution of uncompensated spins [3]. We expected that pressurization would give prominent change on the surface structure and the intra-particle structure resulting in significant
changes on the magnetic properties. Thus, we paid much attention to an iron oxide hydroxide ferrihydrite as a target material for pressure experiment. Ferrihydrite is a natural iron oxide hydroxide mineral with poorly defined crystallinity and varied chemical composition. The structure of ferrihydrite was recently modelled as a packing of clusters constituted of one tetrahedrally coordinated Fe atom surrounded by 12 octahedrally coordinated Fe atoms [4]. Some of formulas have been proposed for its structure (e.g., $5\text{Fe}_2\text{O}_3\cdot9\text{H}_2\text{O}$, $\text{Fe}_5\text{HO}_8\cdot4\text{H}_2\text{O}$) but they are all suited to $\text{FeOOH}\cdot n\text{H}_2\text{O}$ [5-7]. Ferrihydrite originally exhibits antiferromagnetic ordering at $T = 330 \text{ K}$ [8].

2. Experimental

The iron oxide hydroxide ferrihydrite ($\text{FeOOH}\cdot n\text{H}_2\text{O}$) nanoparticles with the particle size of $D = 4.7 \pm 0.2 \text{ nm}$ were prepared according to the procedure mentioned elsewhere [9]. The nanoparticles are grown in an organic-inorganic matrix, which prevents the particles aggregation. The DC magnetic measurements as a function of temperature or magnetic field were performed by using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS-5S) in the pressure region up to $P = 13.5 \text{ kbar}$. Pressure was attained using a piston cylinder cell (CR-PSC-KY05-1, Kyowa-Seisakusho Co., Ltd.), which can be inserted into the SQUID magnetometer [10]. In order to apply pressure effectively, the sample was held inside the teflon cell with the aid of a pressure-transmitting medium, Apiezon-J oil. The pressure was estimated from the load, based on the relation between the load and pressure at liquid helium temperature obtained via previous pressure experiments [10].

3. Experimental Results

Figure 1 (a) shows the temperature dependence of the zero-field cooled (ZFC, open symbols) and field cooled (FC, solid symbols) magnetization measurements in a magnetic field of 1000 Oe of the ferrihydrite nanoparticles with $D = 4.7 \text{ nm}$ at $P = 0$ and 13.5 kbar. The superparamagnetic behaviour can be found in the irreversible behaviour between ZFC and FC processes. The results around the ZFC peak are enlarged in Fig. 1 (b). Herein, the temperature of the ZFC peak position is defined to be $T_{\text{peak}}$, ascribed to a magnetic blocking temperature. The value of $T_{\text{peak}}$ was estimated to be 8.1 K at ambient pressure, decreasing down to 7.5 K at $P = 13.5 \text{ kbar}$. Figure 2 shows the magnetization curves at $T = 7.5 \text{ K}$ for $P = 0 \text{ kbar}$ (a) and 10.0 kbar (b). At least for $H > 10 \text{ kOe}$, the value of magnetization at each field increases with increasing pressure for $P \leq 10.0 \text{ kbar}$. At further pressure, there is no distinct pressure response. In a first approach, the magnetization curve up to 50 kOe can be modeled as the sum of two contributions: (i) a saturation component associated to the uncompensated magnetic moments and (ii) a linear component due to the anisotropy of the uncompensated magnetic moments and to the antiferromagnetic coupled moments [11]. In this frame, the magnetization curve analysis was carried out by using a modified Langevin function with the linear term against the magnetic field $H$, as follows:

$$M = N\left\{\mu L \left(\frac{\mu H}{k_B T}\right) + \chi H\right\}, \quad (1)$$

where $N$ is the particles density, $\mu$ is the particle average uncompensated magnetic moment, $L$ denotes the Langevin function and $k_B$ is the Boltzmann constant. $\chi$ is the magnetic susceptibility per one particle associated to the above mentioned linear component. The broken curve expresses the superparamagnetic saturation component, while the dotted line expresses the linear component. The solid curve shows the fitting result using the modified Langevin function Eq. (1). When fitting parameters such as $N = 1.8 \times 10^{17} \text{ particles/g sample}$, $\mu = 4.2 \times 10^{-19} \text{ emu/particle}$ and $\chi = 1.1 \times 10^{-23} \text{ emu/Oe particle}$ are adopted, we see a good agreement between the experimental data at ambient pressure and the modified Langevin function Eq. (1). The values of $\mu$ and $\chi$ obtained by fitting the magnetization curve under pressures are shown in Fig. 3. When pressure was applied, $\mu$ decreases with approaching pressure to 10.0 kbar. Further pressurization tends to saturate this change. On the
other hand, the pressure dependence of $\chi$ shows a behavior contrary to that of $\mu$. The increase of $\chi$ indicates that the antiferromagnetic contribution increases and/or that the magnetization curve approaches a Langevin style at lower fields, i.e. that anisotropy energy $E_a$ decreases. Together, the decrease of $T_{\text{peak}}$ and the increase of $\chi$ with pressure indicate the decrease of $E_a$, associated to the decrease of $\mu$. Silva et al. have reported that $E_a \propto V^{1/2}$ and $\mu \propto V^{1/2}$ ($V$ being the average particle volume) in the ferrihydrite nanoparticles here studied [3]. In this view, the reduction of $E_a$ and $\mu$ might be triggered by the volume shrinkage under pressure.

Figure 1. (a): Temperature dependence of ZFC and FC magnetizations of the ferrihydrite nanoparticles with $D = 4.7$ nm at $H = 1000$ Oe at $P = 0$ and 13.5 kbar. (b): Enlarged figure of the rectangular area of Fig. 1(a). The arrows indicate the ZFC peak temperature ($T_{\text{peak}}$) for $P = 0$ and 13.5 kbar. The solid curve is a visual guide.

Figure 2. Magnetization curves at $T = 7.5$ K for $P = 0$ kbar (a) and 10.0 kbar (b) of the ferrihydrite nanoparticles with $D = 4.7$ nm. The open circles represent the experimental data. The solid curve represents the modified Langevin function Eq. (1). The dotted line shows the linear contribution, while a broken curve shows the saturation contribution.
Figure 3. Pressure dependencies of the magnitude of the average uncompensated magnetic moment ($\mu$) and the magnetic susceptibility ($\chi$) associated to both the antiferromagnetic coupled moments contribution and anisotropy of the uncompensated magnetic moments ($E_a$) for ferrihydrite nanoparticles with $D = 4.7$ nm.

4. Conclusion

We investigated the effects of pressure on the ferrihydrite nanoparticles with the diameter of 4.7 nm in the pressure region up to $P = 13.5$ kbar. The field dependence of magnetization up to 50 kOe exhibits the coexistence of linear and saturation contributions. A series of analytic data for $P \leq 10.0$ kbar suggest that the particles uncompensated magnetic moment decreases, while the linear contribution increases up to about twice of the initial. At the same time, the maximum of the temperature dependence of the low field magnetization decreases with pressure. Together, these findings indicate the decrease of the anisotropy energy associated to the decrease of particles uncompensated magnetic moment. Future diffraction measurements under pressure may give important information about the structural origin of the decrease of the particles uncompensated magnetic moment.

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