

Pressure effects on hollow iron oxide nanoparticles

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Pressure effects on hollow iron oxide nanoparticles were investigated through XRD experiments and magnetic measurements. The pressure dependence of coercive field H_c exhibited the minimum at around 3 kbar, whereas the saturation moment M_s showed the maximum at around 9 kbar. The effective anisotropy constant K_{eff} , estimated from $K_{\text{eff}} \sim H_c M_s$, did not change below about 4 kbar, and afterward it exhibited a monotonous increase against the increase of pressure. The change in K_{eff} is qualitatively consistent with that of lattice parameter, suggesting that it originated from the structural deformation of especially the surface.

1 Introduction

Pressure is a thermodynamical parameter on which changes in structural and magnetic properties are commonly observed. In the case of nanoparticles (NPs), pressure induces changes in the transition temperature, changes in susceptibility and magnetization, changes in the hysteresis cycles and changes in the effective anisotropy energy barrier. The effect of pressure in the nanoparticles (NPs) can be divided into the effect of core and surface [1-6]. Core/shell models have been successfully used in the context of magnetic properties of maghemite NPs. These models often consider that the particles are constituted by a bulk-like core and a surface (namely shell). The origin of this surface magnetic behavior is associated to incomplete coordination of superficial ions and to the likely occurrence of surface structure defects

Since maghemite core and shell properties have a different pressure response [1, 2], one can expect that maghemite particles with different geometry have a different behavior with pressure, allowing a better insight on the magnetic properties of core and shell [6]. Hollow maghemite NPs are an exotic and interesting system where the relevance of surface was highlighted and where this geometry effect is expected to be apparent [7, 8]. Accordingly, we investigated the effect of pressure in hollow maghemite NPs, and we compared this effect with that observed in solid maghemite NPs obtained by polymeric-assisted synthesis and non-aqueous routes [6]. Herein we report the pressure effect on hollow maghemite NPs.

2 Experiment

Hollow iron oxide NPs were obtained by the nanoscale Kirkendall effect following a previously reported procedure [7]. X-ray diffraction (XRD) measurements were performed at room temperature as a function of pressure up to 30 kbar using a cylindrical imaging plate diffractometer at the Photon Factory of the Institute of Materials Structure Science at the High Energy Accelerator Research Organization (KEK) [9]. The

wavelength of the incident X-ray was $\lambda = 0.68850(2)$ Å. Pressure was applied using a diamond anvil cell, which consisted of two diamond anvils with flat tips of diameter 0.8 mm and a 0.3-mm-thick CuBe gasket. The pressure was calibrated by the ruby fluorescence method [10]. The maghemite NPs and a few ruby crystals were held along with a pressure-transmitting medium (fluorinated oil, FC77, Sumitomo 3M Co., Ltd.) in a sample cavity of diameter 0.4 mm located at the center of the CuBe gasket. The analysis of the diffraction patterns was performed by Rietveld refinement using the FullProf package [11]. The size effects were treated with the integral breadth method using the Voigt model for both the instrumental and intrinsic diffraction peak shape considering a Thompson-Cox-Hastings pseudo-Voigt convoluted with axial divergence asymmetry function to describe the peak shape. The contribution of the finite size of the NPs crystallites to the peaks broadening was taken into account by an isotropic model yielding an average apparent size.

For the magnetic measurements, the pressure was generated by a piston-cylinder-type CuBe pressure cell that was designed to be inserted into a commercial superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS) [12]. The maghemite NPs were held in the Teflon cell, which was installed in the pressure cell along with the pressure-transmitting medium (Apiezon-J oil) and a few pieces of superconductor tin used as a manometer. The pressure at liquid-helium temperature was estimated by the shift in the superconducting transition temperature of tin [13]. The ac magnetic response was measured as a function of the temperature and the frequency of the ac field. Under an ac field of 4.0 Oe, the in-phase and out-of-phase components of a series of first-order harmonic components were detected from the Fourier transform of the SQUID voltage, which was measured after modification of the phase delay due to the eddy current of CuBe at each frequency.

3 Results and Discussion

TEM micrographs of the hollow sample show the expected geometry of core/shell hollow/solid NPs with an average diameter of about 8 nm and a low size dispersion. The iron oxide shell has about 3 nm, being polycrystalline. XRD patterns of the hollow sample show the existence of NPs with a spinel structure consistent with magnetite/maghemite (Fig. 1(a)). The patterns can be well reproduced by considering the $P4_332$ space group and a peak broadening due to finite size effects. The average apparent size at room pressure is about 2.2 nm (Fig. 1(b)), in good accordance with the 3 nm crystalline domains observed by HRTEM. The cell parameter decreases monotonically with pressure, whereas the average apparent size has no defined trend having values in the 2.1 to 2.4 nm range (which is probably close to its error bar).

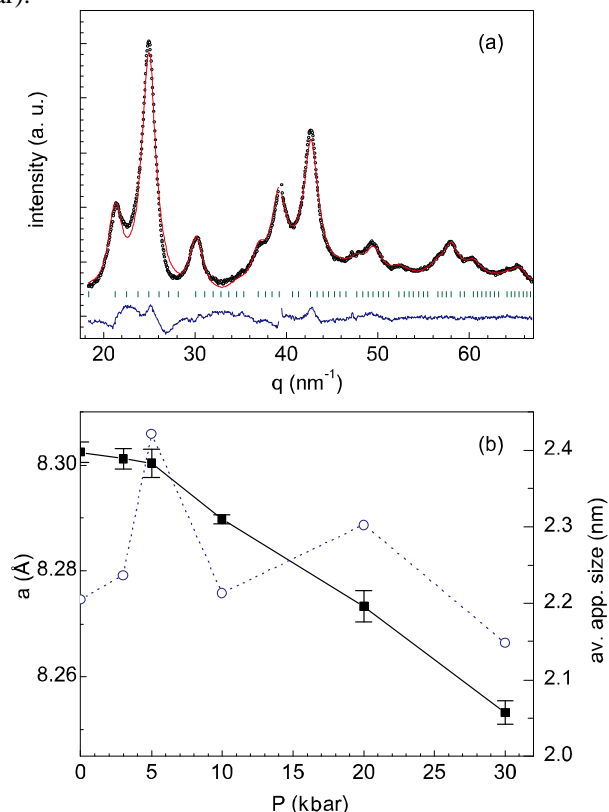


Fig. 1: (a) Room temperature and ambient pressure X-ray diffraction (XRD) pattern of the hollow maghemite NPs. Continuous (red) line corresponds to Rietveld refinement of a spinel as described in the text, vertical lines represent the position of allowed Bragg peaks, while horizontal (blue) line represents the fit residues. (b) pressure dependence of the cell parameter a (left scale, full symbols) and average apparent size (right scale, open symbols); solid lines are eye guides.

At low temperature, magnetization shows hysteresis with field (Fig. 2(a)). The coercive field H_c and the magnetization at the maximum field used in the experiment (denoted as M_s) are pressure dependent, increasing and decreasing with pressure, respectively (Fig. 2(b, c)). Taking into account these two dependencies, it is

possible to evaluate the pressure dependence of the effective anisotropy constant K_{eff} , since $K_{\text{eff}} \sim H_c M_s$. Despite the opposite trends of H_c and M_s , K_{eff} increases with pressure, anticipating a pressure dependence of the anisotropy energy barrier.

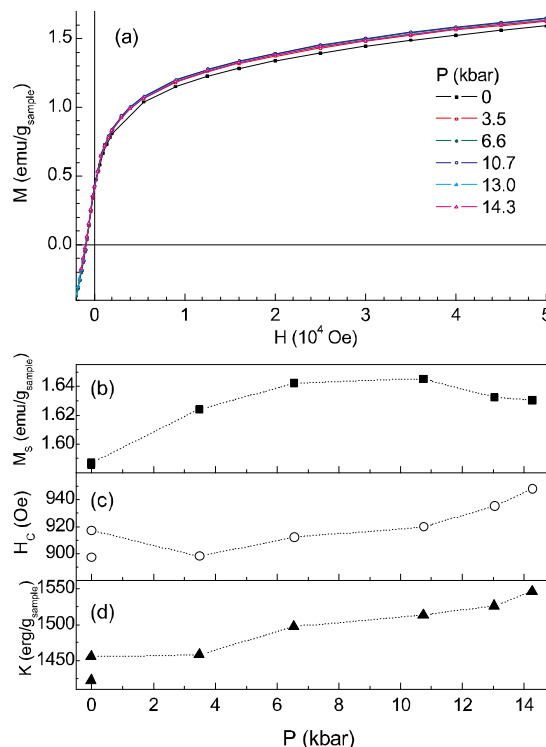


Fig. 2: (a) Field dependence of the magnetization of hollow NPs measured at decreasing fields after zero-field cooling and obtained at selected pressures and $T = 5$ K. Pressure dependence of the (b) magnetization at high field (5×10^4 Oe) M_s obtained at $T = 5$ K, (c) coercive field H_c and (d) effective anisotropy constant K_{eff} . Lines are eye guides for data obtained at increasing pressures. The values obtained at ambient pressure after pressure release are shown as isolated symbols.

Pressure dependence of effective anisotropy constant K_{eff} was qualitatively consistent with that of lattice parameter. It suggested that the pressure response originated from the structural deformation of the surface, which is sensitive to the external strain. In the nano-scale magnet, strain tuning via the particle surface can be a promising approach for artificial manipulation of magnetic properties.

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