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Determination of Core and Surface Magnetic Anisotropy in Maghemite Nanoparticles using Pressure Experiments

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Introduction

Magnetic Property of nanoparticles often differs from that of the bulk material due to finite size and surface effects. It is not straightforward to separate these effects and to investigate the intrinsic origin of the changes associated to the reduction of size. In this report, we show that applied pressure induces structural and magnetic changes on maghemite (γ-Fe_2O_3) magnetic nanoparticles dispersed in a polymer, so that the present study can be used to gain insight on the origin of anisotropy and to separate it into volume and surface contributions [1]. The maghemite nanoparticle consisted of a core with structural periodicity and a disordered shell without the periodicity, and the core exhibited superparamagnetism.

Experimental

The maghemite/polymer nanocomposite used in the present study was prepared by the mixture of poly(vinylpuridine)(PVP) and iron bromide solution, according to the procedure mentioned elsewhere [2]. The nanoparticles size at ambient pressure was estimated by TEM as D_0 = 5.1 ± 0.5 nm. Ac magnetic measurements were performed using a SQUID magnetometer. Pressure was attained using a piston cylinder cell. Synchrotron radiation powder X-ray diffraction (XRD) measurements were carried out at room temperature and pressures up to 27.7 kbar at BL-1B of the Photon Factory of KEK. Pressure was attained using a diamond anvil cell (DAC). The wavelength of the incident X-ray was 0.068831 nm.

Experimental results

Figure 1 shows the ratios of core volume (V_{core}) and shell volume (V_{shell}) to particle volume (V) under pressure for the maghemite nanoparticles. V_{core} was calculated using the diameter of the core (D_{core}), which was calculated from the values of the full-width at half-maximum of the diffraction peak and the diffraction peak angle for the (311) plane using the Scherrer's formula.

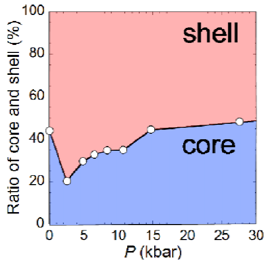

Figure 1. Pressure dependence of the ratios of the core volume and the shell volume to the particle volume in maghemite nanoparticles with D_0 = 5.1 nm.

The residual volume after subtracting V_{core} from V at each pressure corresponds to V_{shell} (= V - V_{core}). V was calculated based on the following assumption: the initial particle diameter, D_0, is 5.1 nm, and the shrinkage ratio for the entire nanoparticle is the same as that of the unit cell in the core under pressure. These ratios, V_{core}/V and V_{shell}/V, are considered to be the same as the ratios of the number of Fe^{3+} ions constituting the core and shell to that constituting the entire particle. The experimental results indicated that the number of Fe^{3+} ions constituting the core was reduced to a half of the initial value at 2.5 kbar, and increased at pressures above 2.5 kbar.

For 2.5 $\leq P \leq$ 10.7 kbar, the shrinkage of V is small, and the change of the ratios, V_{core}/V and V_{shell}/V, appears dominantly. Thus, activation energy barrier between spin-up and spin-down states estimated from ac magnetic measurements, ΔE (P), was plotted against $V(P)$ and $V_{core}(P)$ as Fig. 2. We found that ΔE is approximately proportional to V_{core} (P). In the core-shell model, surface anisotropy (K_S) is sometimes relevant, being expressed as an extra term, such as $\Delta E = K_{core}V_{core}+K_S S$. Here, K_{core} is the effective anisotropy constant per unit volume of the core, and S is the surface area of the particle. From the slope of the curve for 2.5 $\leq P \leq$ 10.7 kbar, $K_{core} = 7.7\times10^5$ erg/cm^3. At the same time, ΔE extrapolates to 246 ± 10 K at V_{core} = 0, corresponding to the energy barrier associated to the shell. Considering D = 5.0 nm for 2.5 $\leq P \leq$ 10.7 kbar, one could determine $K_S = 4.2\times10^{-2}$ erg/cm^2.

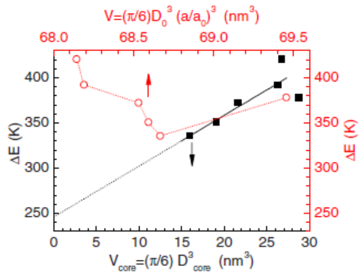

Figure 2. Activation energy barrier ΔE as a function of V_{core} and V. Solid line represents the best linear fitting to ΔE (V_{core}) and dotted line its extrapolation for V_{core} = 0 for 2.5 $\leq P \leq$ 10.7 kbar. a is the cell parameter, and a_0 is the initial value of a at ambient pressure.

References

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