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EXAFS Studies on Nanoparticulate Ferrite Hollow Spheres

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1 Introduction

A superparamagnetic-type blocking process are observed in sub-micron-sized hollow spheres assembled from MFe_2O_4 (M=Ni, Mg) nanoparticles. Furthermore, a spin-glass-like behavior due to surface spin freezing is found in Ni-ferrite nanoparticles. The magnetic field dependence of the surface spin freezing temperatures is different between the ordinary nanoparticles and the fabricated nanoparticlulate hollow spheres[1]. The surface spin freezing is subject to the influence of the inter-particle interactions in the hollow sphere nano magnet, but also the local environments of the Ni and Fe ions in the surface of nanoparticle. In this report, we investigate the local structures around Ni and Fe ions by measuring Ni, Fe-K edge EXAFS spectra.

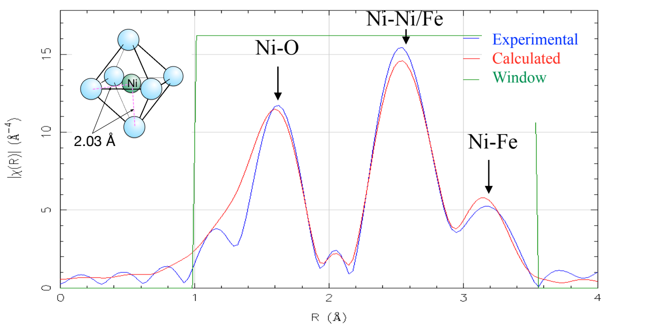
2 Experiment

Nanocrystalline ferrites were synthesized by using the co-precipitation method. Hollow spherical ferrite nano structures were prepared through a template method. The morphology and the structures of the products were determined by using TEM and X-ray diffraction. The sizes of these small nanoparticles are 6-10 nm for Ni ferrite. The mean diameters of hollow the spheres are estimated to be 291 nm, and the thickness of shells are about 13 nm. The K-edge EXAFS spectra were recorded in transmission mode at the facilities of XAFS beam line BL-9C in PF-KEK. The EXAFS data were processed by Athena and Artemis software packages.

3 Results and Discussion

The EXAFS Fourier transforms obtained at the room temperature for $NiFe_2O_4$ are shown in Figure 1. Bulk $NiFe_2O_4$ particles have a inverse spinel structure in which all the Ni^{2+} ions occupy octahedral sites (B-site). Half of the Fe^{3+} ions preferentially occupy tetrahedral sites (A-site) and the rest fill octahedral sites (B-site). The fitting procedure in the EXAFS analysis result in a contribution from Ni-O bond length at 2.03 Å for bulk sample (see phase corrected values in Table 1). These results are in qualitative agreement with the earlier findings by Varskoi *et al.*[2]. In contrast, the Fourier transform in hollow sphere sample show significant difference, indicating that the structural environment around Ni^{2+} is different. The first peak near 1.66 Å is due to one Ni-O bond distance, which is appreciably shorter than the corresponding Ni-O bond length (2.03 Å) of octahedral site in a $NiFe_2O_4$ spinel lattice. This results suggest that a distortion and an oxygen-deficient as in Fig.1 are occurred in NiO_6 octahedron at the surface of fine particles.

(a) bulk



(b) hollow sphere

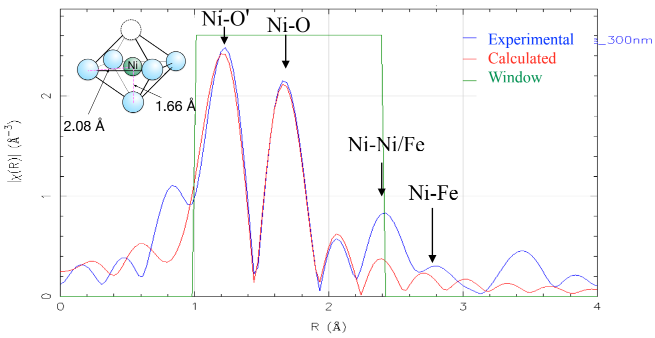


Fig. 1: Fourier transforms of Ni K-edge EXAFS spectra for $NiFe_2O_4$; (a) bulk and (b) hollow spheres with 300 nm in diameter. The inter-atomic distance R is close to near position by phase shift in Fourier transform process (see phase corrected values in Table 1).

Table 1: Results of the EXAFS Ni K-edge curve-fitting for Ni ferrite

	Ni-O		Ni-Ni/Fe		Ni-Fe	
	r /Å	N	*r* /Å	N	*r* /Å	N
bulk	2.03	5.7	2.93	5.7	3.46	5.7
Hollow sphere	1.66 2.08	0.9 3.9	2.43	—	3.25	—

References
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