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Fe *K*-edge XAFS study of magnetite nanoparticles

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Introduction

Magnetite(Fe_3O_4) has long been recognized as an important magnetic material. Recently its nanoparticles are also used in medical and biotechnical applications. Magnetic nanoparticles show superparamagnetism when thermal disturbance exceeds magnetic anisotropy energy. The structure and the electronic structure at the surface of nanoparticles have major influence on their magnetic properties. We performed XAFS measurements of nanoparticles which show different blocking temperatures, corresponding to different size and surface modification.

Experiments

Magnetite nanoparticles were synthesized by microemulsion and coprecipitation method[1][2]. All samples are dispersed in graphite powder, and pressed into pellets. For each measurements, pellets were installed in a cryocooler, and the samples were cooled from 95K to 300K. Fe *K*-edge XAFS measurements are carried out at BL-12C beam line of KEK-PF. Synchrotron radiation was monochromatized using Si(111) crystals. Athena computer code was used to extract-EXAFS oscillations from the data[3].

Results and discussion

Figure 1 shows FT-EXAFS data at 95K obtained for the magnetite nanoparticles and bulk reference (Fe_3O_4, γ-Fe_2O_3) samples. The peaks at 2.7Å and 3.2Å correspond to B-site Fe-Fe shell and between A-site and A-site Fe-Fe shell, respectively. The magnitude of these peaks decrease as the particles size becomes smaller.

If we assume simple truncation size effect on reduction of the coordination number, the simulation cannot describe the reduction of the second and third peak. This indicates substantial structural disorder at the surface of the nanoparticles.

Figure 2 shows temperature dependence of magnetite nanoparticle (2nm) EXAFS spectra. In order to distinguish thermal disorder from structural ones, we evaluate the ratio of peak height (second and third peak) at 300K to 95K. The results are shown in Table 1. No significant difference was found between these samples. Thus, these are no large difference in the lattice vibration between bulk and nanoparticle samples. Consequently, large static disorder exists at the surface of nanoparticles. This disorder may be related to the changes in the magnetic anisotropy i.e. the blocking temperature.

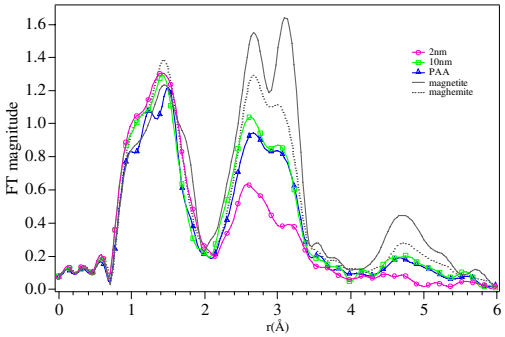

Figure 1. Fe *K*-edge FT-EXAFS spectra of magnetite nanoparticles and bulk reference(Fe_3O_4, γ-Fe_2O_3) samples at 95K

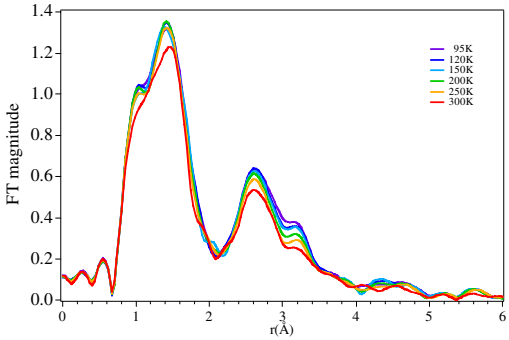

Figure 2. temperature dependence of magnetite nanoparticle(2nm) EXAFS spectra

Table 1: peak height ratio
[peak height at 300K] / [peak height at 95K]

sample	Second peak	Third peak
bulk	0.838	0.674
10nm	0.847	0.690
10nm coated with PAA	0.871	0.666
2nm	0.837	0.673

References

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