

Local structure of Ni hydroxide cluster synthesized by the microemulsion method

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Introduction

Although metal compound clusters are expected to have unique physicochemical properties, they are often unstable under atmospheric condition. Recently, the microemulsion method has been developed, in which clusters are synthesized in micro-spaces inside inverse micelles and protected by surfactant molecules. The clusters are often self-assembled to form a super-lattice structure called 'nanocrystal'. Using this method, we synthesized Ni hydroxide clusters, and measured their magnetization by SQUID. Although the bulk sample of Ni hydroxide shows antiferromagnetism, the synthesized cluster shows a hysteresis curve in the field-dependent magnetization below 10K. This behavior is interpreted by super-paramagnetism; although spin's magnetic moment is oriented to one direction in each cluster, no magnetic interactions operate between them. In this work, we measured and analyzed Ni *K*-edge XAFS spectra of Ni hydroxide clusters, and from these results, we discussed the correlation between their structures and magnetic properties.

Experimental

Xylene solution of a surfactant (diisooctyl sodium sulfosuccinate (AOT)) were added to 0.1 mol/l Ni(NO₃)₂ aqueous solution. Then 0.1 mol/l KOH aqueous solution was poured into the solution and was stirred. Ni hydroxide clusters were obtained from an organic phase. In the microemulsion method, the cluster size is controlled by the molar ratio of a surfactant. These clusters are too small to measure the powder x-ray diffraction quantitatively. And they are so easily damaged by high-energy electron beam that TEM images could not be obtained. Ni *K*-edge XAFS spectra were measured at 16-18 K with the transmission mode at BL-9A using a Si(111) double-crystal monochromator. Sample powders were diluted by BN and pressed into disks.

Results and Discussion

Ni *K*-edge XANES of Ni hydroxide cluster are almost identical with that of the bulk compound, revealing that the electronic structure around Ni atoms does not change as the cluster size becomes smaller. Fig. 1 shows Fourier transforms of Ni *K*-edge EXAFS spectra, and Table 1 lists the interatomic distances obtained from the EXAFS analysis. The results indicate that the cluster's distances of Ni-O1 and Ni-Ni1 become shorter and the coordination numbers of O2,3 are smaller.

The bulk Ni hydroxide consists of a stack of 2-D Ni(OH)₂ sheet (see Fig.2). In the 2-D sheet, there are ferromagnetic interactions between Ni atoms. On the other hand, they exhibit an antiferromagnetic coupling between two adjacent sheets, leading to bulk antiferromagnetic property. From the difference in local structure and magnetization between bulk and cluster, we interpret the clusters as a 2-D monolayer-like structure. Since single 2-D monolayer possesses a ferromagnetic character, synthesized sample on the whole shows super-paramagnetism. The single 2-D monolayer has a smaller coordination number, which might be closely related to the reduction of the Ni-O1, Ni-Ni1 distances.

Table 1 Interatomic distances (Å) which are obtained from the EXAFS analysis. Number in () shows errors of the last digit.

Sample	Ni(OH) ₂ standard	Ni(OH) ₂ cluster
Ni-O1	2.074(9)	2.060(7)
Ni-Ni1	3.129(3)	3.088(4)

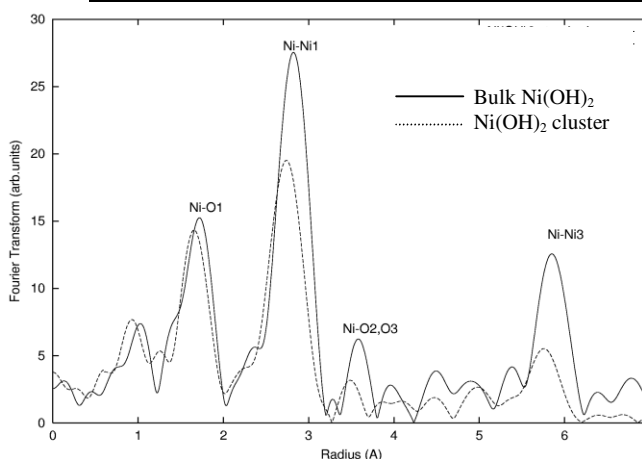


Fig.1 Ni-K edge EXAFS Fourier transform

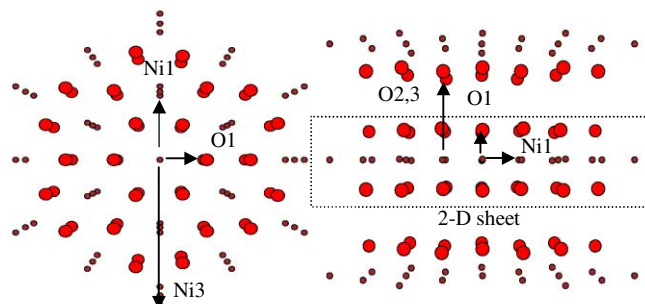


Fig.2 The structure of Ni(OH)₂ crystal (right: [010] direction, left: [001] direction) large circles: O, small circles: Ni, H is omitted. Dotted line: 2-D sheet

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