

Local structures of nano-structured Fe clusters

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Introduction

The structural properties of nano-metals are of interest in the variety of fields in solid-state physics and chemistry. Their structural properties influence on their physical and chemical properties, such as the enhancement of chemical reactivity, the lowering of the melting temperature, and the magnetic behavior. We have succeeded to synthesize the metallic nickel colloids with nano-porosities [1]. The XAFS studies on the nickel colloids have been performed and have elucidated that the colloids have a characteristic local structure. Recently, we also have synthesized the nano-structured iron clusters (nano-Fe) that are stable in atmosphere. The clusters are too small to characterize their structures by diffraction techniques. The TEM photographs of the clusters cannot be obtained, because they are unstable under the irradiation of the electron beam. In this work, we report an investigation on the structural properties of nano-Fe by Fe *K*-edge XAFS spectra.

Experimental

The FeCl₃ were dissolved in the aqueous solution of poly(vinylalcohol) (PVA). The NaOH aqueous solution was pored into the mixed solution of Fe³⁺ ions and PVA polymers at 353 K. The precipitations were obtained and were separated by filtration. The precipitates were dried at room temperature after washing with distilled water. The dried precipitates were heated at 973 K under nitrogen gas flow. The nano-Fe has been obtained by the thermal decomposition of Fe³⁺/PVA composites. The XAFS measurements were performed on Fe *K*-edge at BL-7C beam line with transmission mode. Samples were adjusted in a sufficient quality to give an edge jump. The program code FEFF8 was used to calculate the theoretical phase and amplitude for curve fitting.

Results and Discussion

The XANES spectrum of nano-Fe became a broadening compared with that of Fe foil, owing to a consequence of the cluster-size distribution [2]. The radial distribution functions (RSFs) calculated from the EXAFS signals for the Fe foil and the nano-Fe are shown in Figure 1. Although these RSFs show few peaks coming from the scattering of neighboring Fe atoms, the intensity of the peaks in the nano-Fe was smaller than that in the Fe foil, suggesting the decrease in the amplitude of the $\chi(k)$ related to the structural parameters. The

structural parameters are calculated from the EXAFS data by curve fitting the first peak of the RSF. Table 1 shows the coordination number (*N*), nearest-neighbor interatomic distance (*R*), Debye-Waller factor (σ) of the Fe foil and the nano-Fe. The σ value of the nano-Fe was larger than that of the Fe foil, suggesting the degradation of the structures in Fe clusters. The drastic decrease in the *N* of the nano-Fe was also observed, owing to the formation of the very small clusters. Because small clusters with nano-dimensions have a significant fraction of the atoms located on the surface, the RSF shows a reduction in the coordination numbers.

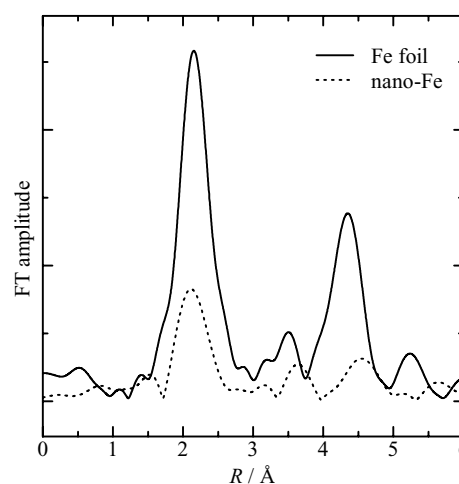


Figure 1. The radial distribution functions of Fe foil and nano-Fe.

Table 1: The local structural parameters of Fe foil and nano-Fe.

	<i>N</i>	<i>R</i> / Å	σ^2 / Å ²
Fe foil	8.15	2.52	0.00443
Nano-Fe	2.73	2.51	0.00716

References

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[2] A. Balerna et al., *Phys. Rev.*, B31, 5058 (1985).

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