

Coordination study of rare earth elements on Fe oxyhydroxide and Mn dioxides: Part I. Influence of a multi-electron excitation on EXAFS analyses of La, Pr, Nd, and Sm

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ABSTRACT

Coordination states of rare earth elements (REEs) adsorbed by iron oxyhydroxide (FeOOH) and manganese dioxide (δ -MnO₂) (REE = La, Pr, Nd, and Sm) were determined using extended X-ray absorption fine structure (EXAFS) spectroscopy. Multi-electron excitation, resulting in double-electron excitation ($2p, 4d \rightarrow 5d, 5d$) for REE- L_{III} edge EXAFS spectra, possibly causes a considerable error in EXAFS analyses for light REEs. To obtain reliable structural parameters this study elucidates the effects of double-electron excitation on the local structure determination of light REEs on poorly crystallized FeOOH and δ -MnO₂. For this study, anomalous features attributable to excitation are superimposed on EXAFS signals of La, Pr, Nd, and Sm samples in the 5.0–7.0 Å⁻¹ k range. The relative intensity of the double-electron excitation to the L_{III} adsorption edge is <1.1%. Consequently, the double-electron excitation engenders a smaller error than those estimated in fitting for Pr, Nd, and Sm samples. However, significant correction is necessary for the determination of local coordination states of La samples: interatomic distances are 0.007–0.036 Å shorter after correction. The EXAFS analyses of REE-sorbed Fe samples show that adsorbed La, Pr, Nd, and Sm have a mixture of eightfold and ninefold coordination structures and form inner sphere complexes at the FeOOH surface. The determined structural parameters of light REE-sorbed δ -MnO₂ suggest that adsorbed light REEs have distorted tenfold-coordination spheres consisting of six short and four long REE–O bonds and form inner sphere complexes. Their coordination structures are more disordered than those of aquo ions and FeOOH samples.

Keywords: X-ray absorption spectra, rare earth elements, iron oxyhydroxide, manganese dioxide, multi-electron excitation, local coordination state, inner sphere complex, outer sphere complex