

Influence of multi-electron excitation on EXAFS spectroscopy of trivalent rare-earth ions and elucidation of change in hydration number through the series

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ABSTRACT

We have made a detailed study of the extended X-ray absorption fine spectra (EXAFS) at the K edge of aqueous Y ion and at L_3 edges of aqueous lanthanide ions and thereby elucidated the systematic changes in their hydration structures. Anomalous peaks arising from double-electron excitation ($2p, 4d \rightarrow 5d, 5d$) appear in the EXAFS signals of La^{3+} - Tb^{3+} between $5\text{--}7 \text{ \AA}^{-1}$. We established a removal process of double-electron excitation from EXAFS spectra. Using that process, we confirmed that the intensity and energy position of the extracted double-electron excitation are comparable to previously reported data. The presence of double-electron excitation engenders a smaller error than the errors estimated in the fitting process. Consequently, double-electron excitation does not seriously affect the determination of the structures of REE^{3+} aquo ions in the first coordination sphere. Subsequent EXAFS analyses of hydrated REE^{3+} ions suggest that the hydration numbers, the interatomic distances, and the Debye-Waller factors decrease from 9.7, 2.55 Å, and $9.0 \times 10^{-3} \text{ \AA}^2$ for La^{3+} to 7.9, 2.31 Å, and $5.7 \times 10^{-3} \text{ \AA}^2$ for Lu^{3+} . These parameters change as a sigmoid curve with increasing atomic number. The hydration structures of REE^{3+} ions are inferred to change from the nonhydrated structure for La^{3+} - Nd^{3+} to the octahydrated structure for Tb^{3+} - Lu^{3+} through intermediate structures for Sm^{3+} , Eu^{3+} , and Gd^{3+} . In addition, the hydration state of Y^{3+} closely resembles that of Ho^{3+} because the two have almost identical ionic radii.

Keywords: EXAFS, rare-earth elements, multi-electron excitation, hydration structure, structural change