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Report

Considering the importance of Cr in geosciences and catalysis it is of paramount interest to many researchers to develop alternative techniques to study the Cr electronic structure and local coordination. High energy resolution X-ray emission spectroscopy is ideally suited to address this important issue.

A set of appropriate reference spectra for different oxidation states and local symmetries at the Cr sites was collected on the ID26 beamline. High energy-resolution emission detection was achieved by employing a spherically-bent Si crystal with a (333) orientation in Rowland geometry at Bragg angles between 82 to 86 degrees. An avalanche photo diode (APD) was used as a fast detector for emission detection to avoid non-linear effects. Some selected XANES spectra normalized to the edge jump are displayed in figure 1. Figure 2 clearly reveals that using resonant inelastic X-ray scattering the K absorption pre-edge features can be investigated far more detailed than in conventional XANES measurements. The Cr 1s3p RIXS data were obtained following a published protocol (Glatzel and Bergmann, 2005), taking advantage of the quick scan modus available at ID26.

In the analysis of pre-edge features, a baseline subtraction was performed by fitting an arctangent function on the edge. Gaussian profiles were then used to determine the energy position of pre-edge components. A clear relation has been found between the integrated intensity vs centroid position, the oxidation state and local coordination environment.

Furthermore, the obtained spectra are used to establish a detailed understanding of the 1s $\rightarrow$ 3d pre-edge feature and its sensitivity to the electronic structure at the Cr site. In previous studies, the K pre-edge features of Mn and Fe could be explained based on a crystal field multiplet approach (Glatzel et al., 2004; Westre et al., 1997) and similar calculations are in progress for Cr in collaboration with Riccardo Gusmeroli (University of Milano, Italy). Insights into crystal field splittings, two-electron interactions as well as oxidation and spin state are gained.

Our results will set the basis for future studies, in particular for *in situ* experiments in catalysis and geosciences.

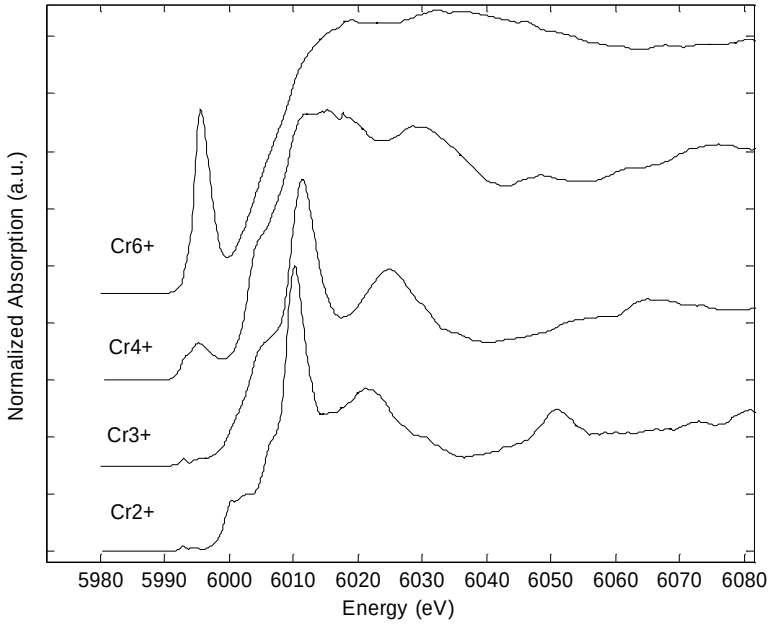

Figure 1: Normalized Cr K-edge XANES spectra of some reference compounds

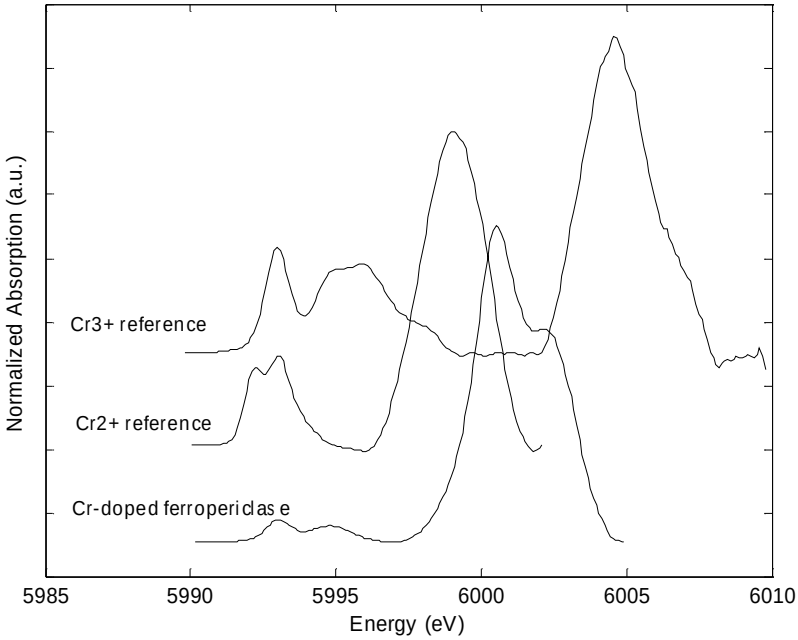

Figure 2: Pre-edge peaks of a Cr^{3+} reference, Cr^{2+} reference and Cr-doped ferropericlase sample after baseline subtraction

References

Glatzel, P., and Bergmann, U. (2005) High resolution 1s core hole X-ray spectroscopy in 3d transition metal complexes - electronic and structural information. Coordination Chemistry Reviews, 249(1-2), 65-95.

Glatzel, P., Bergmann, U., Yano, J., Visser, H., Robblee, J., Gu, W., Groot, F.M.F.d., Pecoraro, V.L., Christou, G., Cramer, S.P., and Yachandra, V.K. (2004) The Electronic Structure of Mn in Oxides, Coordination Complexes and in the Oxygen-Evolving Complex of Photosystem II Studied by Resonant Inelastic X-Ray Scattering (RIXS). Journal of the American Chemical Society, 126(32), 9946-9959.

Westre, T.E., Kennepohl, P., DeWitt, J.G., Hedman, B., Hodgson, K.O., and Solomon, E.I. (1997) A multiplet analysis of Fe K-edge 1s->3d pre-edge features of iron complexes. Journal of the American Chemical Society, 119(27), 6297-6314.