Site-Selective EXAFS Spectroscopy

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Conventional fluorescence-detected EXAFS spectroscopy is element specific but averages over all chemical forms of an element.[1] It is desirable to extend the selectivity of EXAFS spectroscopy to mixed-valent compounds, i.e., compounds that contain one element in different chemical forms. This is possible by taking advantage of the chemical dependence of x-ray fluorescence lines to record site-selective fluorescence-detected absorption spectra.[2] We used the chemically sensitive Kβ fluorescence emission to record Fe K-edge absorption spectra of the high-spin (HS) and low-spin (LS) site in Prussian Blue ($Fe_4(Fe(CN)_6)_3$). The Kβ spectra were recorded at the BioCAT beamline 18-ID at the Advanced Photon Source. A large-acceptance crystal-array analyzer was employed to record the fluorescence emission.[3] The Kβ spectra of ($Fe_4(Fe(CN)_6)_3$ as well as Fe_2O_3 and $K_4Fe(CN)_6$ as models for the HS and LS site are shown in Fig. 1.

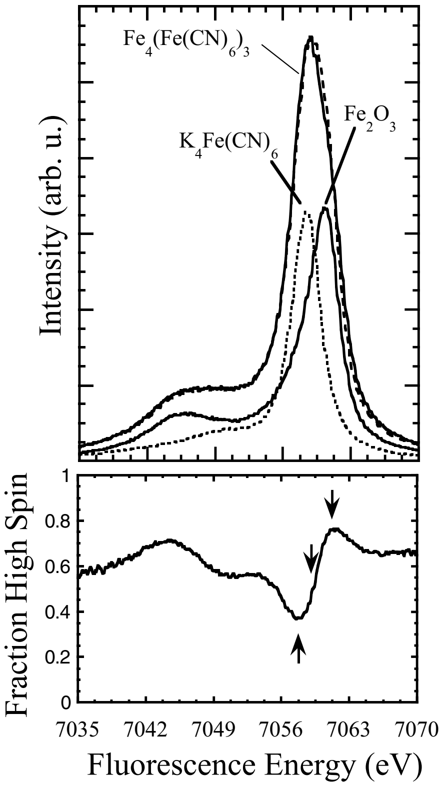

FIG. 1. Kb spectra.

Fe_2O_3 and $K_4Fe(CN)_6$ were used to determine an approximate HS/LS ratio in the Kβ spectrum of Prussian Blue, as shown in Fig. 1, lower panel. Three fluorescence-detected EXAFS spectra were taken at the fluorescence energies indicated in Fig. 1, as well as a non-site-selective EXAFS spectrum in transmission mode. The HS/LS ratio obtained from the models was used to deconvolute the experimental data in a least square fit and to obtain the best approximation of the ‘pure’ EXAFS at the HS and LS site, respectively. The deconvoluted site-selective Fourier filtered and k-weighted EXAFS data are shown in Fig. 2. For the EXAFS fit (dotted lines in Fig. 2), multiple scattering has to be included. EXAFS analysis of the site-selective spectra and curve-fitting data analysis yield the crystallographic distances and physical Debye-Waller factors. We therefore conclude that site-selective EXAFS spectroscopy is a viable tool to study mixed-valent compounds.

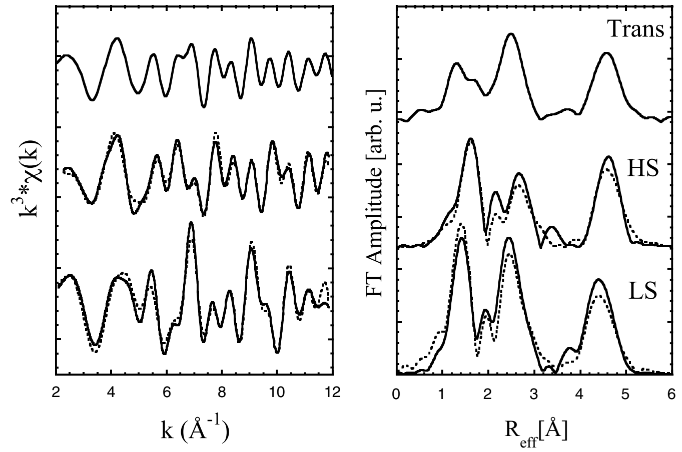

FIG. 2. Site-selective EXAFS in Prussian Blue.

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