HE2315 – Report

Angular dependence of the pre-edge features in reference single crystals as studied by Fe K-edge absorption and emission spectroscopy

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The angular dependence of the pre-edge features in reference single crystals was studied by Fe K-edge absorption and emission spectroscopy. The single crystals used were hematite [α-Fe_2O_3], siderite [$FeCO_3$], almandine [$Fe_3Al_2(SiO_4)_3$] and andradite [$Ca_3Fe_2(SiO_4)_3$].

High energy resolution emission detection was achieved by employing a spherically bent Si crystal with a (531) orientation in Rowland geometry (R = 1034 mm). An avalanche photo diode (APD) was used as a fast detector for emission detection to avoid non-linear effects. The spectra were recorded by selecting the Kβ fluorescence line of iron while scanning the incident energy using the high energy resolution emission spectrometer of the ID26 beamline. At the same time, standard fluorescence XANES spectra were taken with a Si photodiode.

The preliminary set of data for hematite (trigonal crystal system and Fe^{3+} in six-fold coordination) was extended by spectra recorded with the X-ray beam impinging on the (001) plane of the crystal which was positioned at 45^o with respect to the incoming beam. The crystal was then rotated in steps of 30^o up to 180^o. As a consequence, a full three-dimensional picture of the angular dependence of the pre-edge features has been achieved.

In siderite (trigonal crystal system), ferrous iron is located in slightly disordered octahedra that are exclusively corner-linked through the oxygen anions of the carbonate groups. Spectra were collected with the X-ray beam impinging on the (001) plane (and the (110) plane in vertical direction) of the crystal which was positioned at 45^o with respect to the incoming beam. The crystal was then rotated in steps of 30^o up to 90^o. A second set of spectra were collected with the X-ray beam impinging on the $(11\bar{2}0)$ plane (z axis in vertical direction). The orientation of the electric vector was changed in steps of 10^o going from parallel to perpendicular to the y axis.
The large variations in the pre-edge features of siderite depending on the crystal orientation are shown in figure 1.

Almandine and andradite are both garnets which crystallise in the cubic system. In almandine, ferrous iron occurs in an eight-fold coordination site whereas in andradite ferric iron is in a regular octahedron. For both crystals, spectra were recorded with the X-ray beam impinging on the (110) plane of the crystal which was positioned at 45^o with respect to the incoming beam. The crystal was then rotated in steps of 30^o up to 180^o.
The normalised Kβ collected XANES spectra are displayed in figure 2 and 3 for almandine and andradite, respectively. In almandine the pre-edge features do not change as a function of orientation, hence reflecting weak quadrupole interactions (Glatzel et al. 2007). Interestingly, in andradite, pre-edge features even occur for Fe^{3+} at the regular O_h site. Furthermore, in this cubic crystal these features vary as a function of crystal orientation.

Finally, figure 4 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 variations in the pre-edge features as a function of crystal orientation are now being used to rationalize on a mathematical basis how each component of the pre-edge peak varies and thus to quantify the orientation effects on the measured pre-edge features for each model compound. This a priori knowledge will allow the use of data from microscopic single crystals, and thus to correctly interpret micro-XANES data. Evidently, without taking the orientational dependence of pre-edge peak shape and intensity into account, large biases can be introduced on the Fe oxidation state.

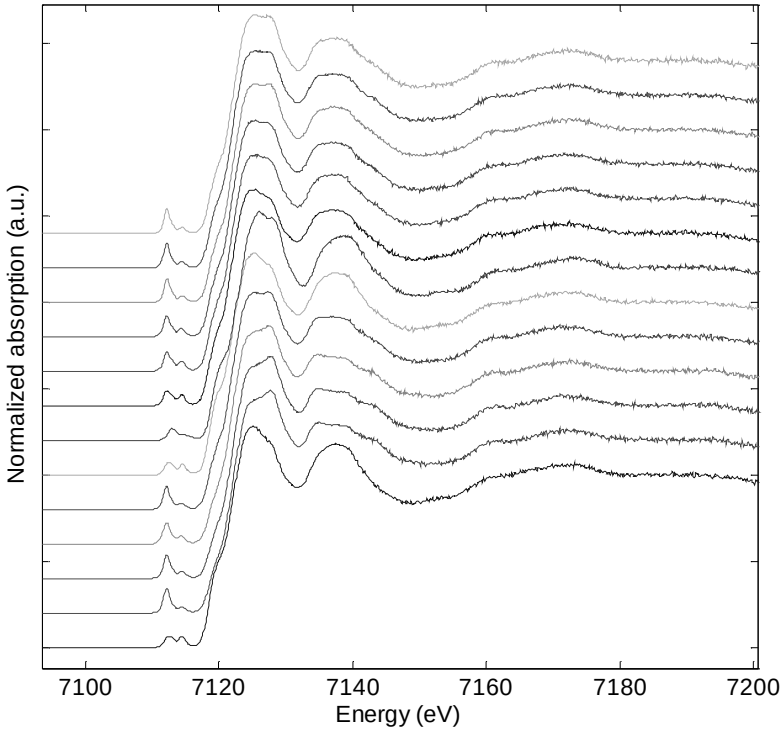

Figure 1: Angular dependence of siderite single crystal as described in text. The Kβ detected XANES spectra were normalized to the edge jump.

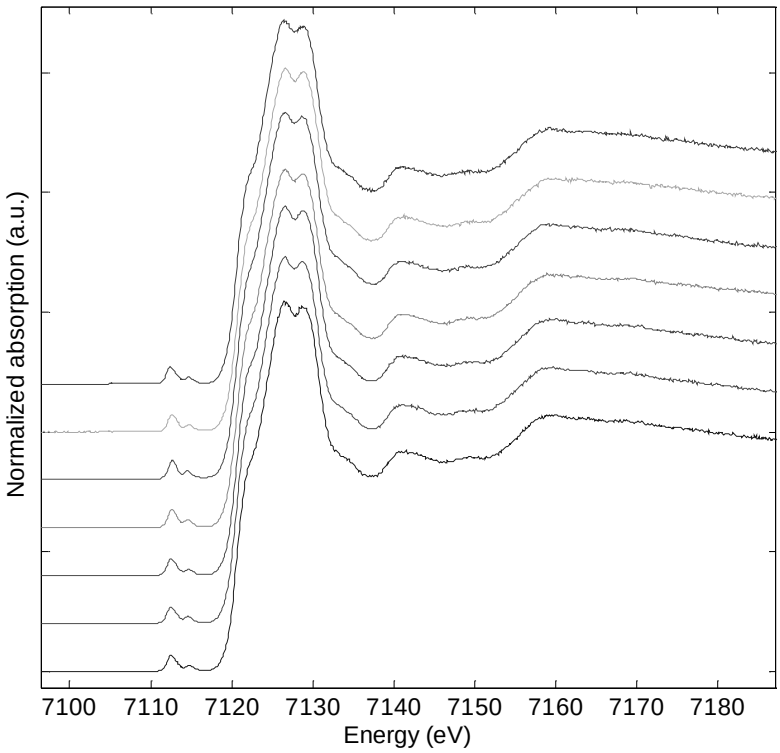

Figure 2: Angular dependence of almandine single crystal as described in text. The Kβ detected XANES spectra were normalized to the edge jump.

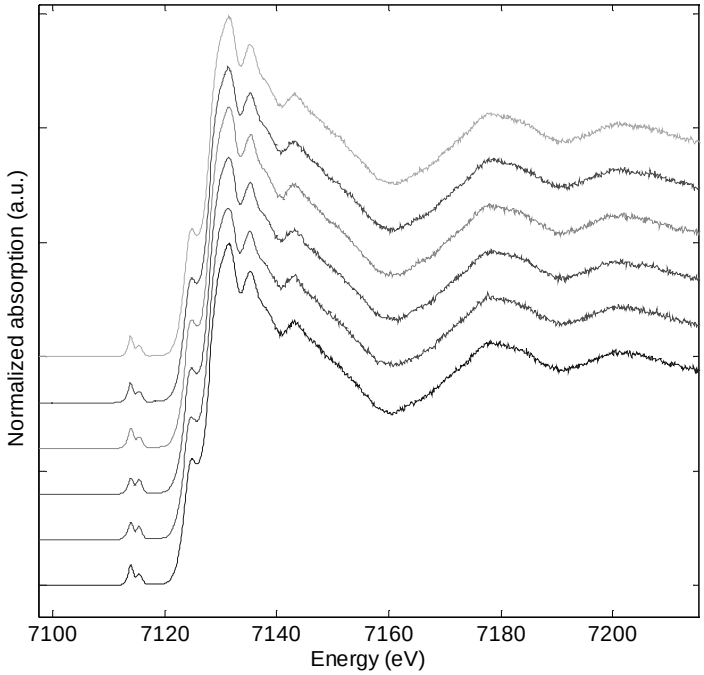

Figure 3: Angular dependence of andradite single crystal as described in text. The Kβ detected XANES spectra were normalized to the edge jump.

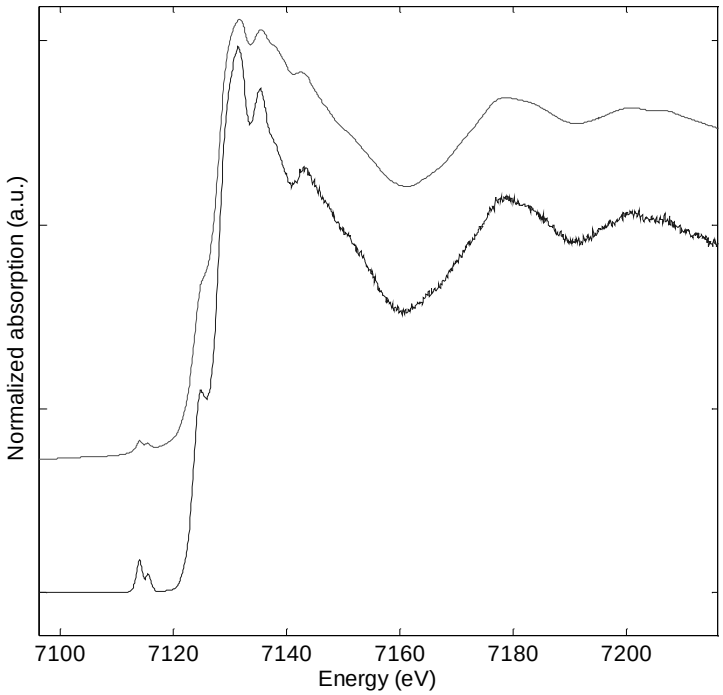

Figure 4: Comparison between Kβ detected (bottom) and conventional XANES (top) measurements. The spectra were normalized to the edge jump.

References:
Glatzel, P., Mirone, A., Eeckhout, S.G., Sikora, M. and Giuli, G. (2007) Orbital hybridization and spin-polarization in the resonant 1s photoexcitations of α-Fe_2O_3. PRL (Submitted)