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Application of the X-ray absorption fine structure (XAFS) in functional and environmental materials

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X-ray absorption fine structure (XAFS) contributes towards understanding functional materials and environmental samples because necessarily targets a specific chemical element. X-ray absorption near edge structure (XANES) helps identify phases and oxidation states. In the extended region (EXAFS) it allows clarifying configurations and angles between the crystallographic directions. Of particular interest is the possibility of tuning the experiment on several elements in the same sample, allowing better elucidate the interatomic distances and order-disorder situations.

The inorganic solid solution γ -Fe_{2-x}Cr_xO₃, maghemite for x=0.75, 1 and 1.25, was studied by X-ray absorption fine structure (XAFS) of K-absorption edge of two elements and by synchrotron radiation X-ray diffraction (XRD).

At first, high-resolution XRD patterns were processed by means of the Rietveld method, using Fullprof [1]. In Rietveld refinements, the ordered/disordered degree of the considered solution is indiscernible in cases of atoms being neighbors in the Periodic Table. Crystallographic interpretation of magnetic and ferroelectric phenomena is shortened by this limitation.

Double-element XAFS analysis was applied to clarify, via short-range structure characterization, the nature of the investigated system. XAFS would confirm or reject the random character of the solution. Measurements were performed at the Stanford Synchrotron Radiation Lightsource at room temperature, at beam lines 2-3 and 4-3. Athena and Artemis codes as interfaces for IFEFFIT [2] and FEFF8.4 [3] codes were employed for XAFS spectra interpretation.

γ -Fe_{2-x}Cr_xO₃ was investigated by XAFS in both Fe and Cr K-edges. Pre-edge decomposition and theoretical modeling of XANES transitions were performed. Interatomic distances were determined for x=1, by the fitting of average spectra in the EXAFS region in both edges simultaneously. In the model the Cr³⁺ as cation t2g3, occupies only the octahedral positions, while Fe³⁺, a cation t2g3 eg2 in a high-spin configuration, occupies both octahedral and tetrahedral positions. By analysis of the Cr K-edge XANES, it has been confirmed that Cr is located in an octahedral environment (Figure 1). These considerations forced fit the spectra with the central atom of Fe being able to occupy two different positions, each with a weight adjustment, while Cr occupies only one. The results of fitting the experimental spectra with theoretical standards made it possible to show that the cation vacancies tend to be located orderly within the structure of the iron-chromium maghemite (FeCrO₃) at sites L2, L3, L5, L6, L8, L9, L11 and L12 (see Figure 2) [4].

Based on the treatment of experimental data from Cr oxides (Figure 3), the study of environmental samples is presented. Arsenic assessment in soil, actinide ion sorption at the interphase solid/aqueous solutions, chromium removal through membranes, and many other subjects have been studied by means of XANES and EXAFS. Figure 4 shows the μ -XAFS spectra from the surface impurities of crystals from the Naica mine. Phases in trace amounts were identified.

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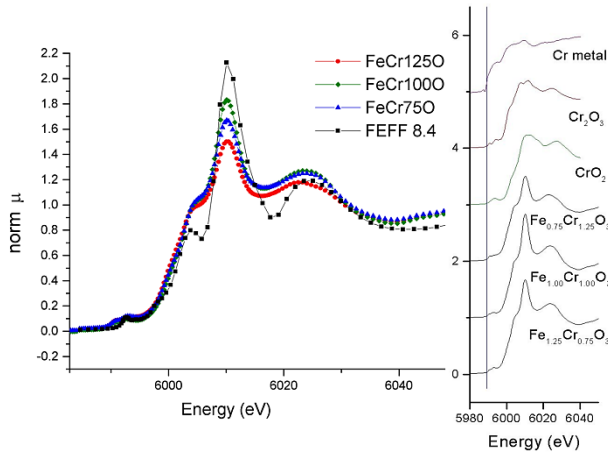


Figure 1. Cr K-edge XANES. The first inflection of the main edge in maghemite samples are at 5998.2, 5999.4 and 5998.8 eV, for Cr contents $x = 0.75, 1.00$ and 1.25 , respectively; and Cr_2O_3 and CrO_2 are at 5999.4 and 6001.3, respectively. Also, the pre-edge peak is practically vanishing in maghemite spectra.

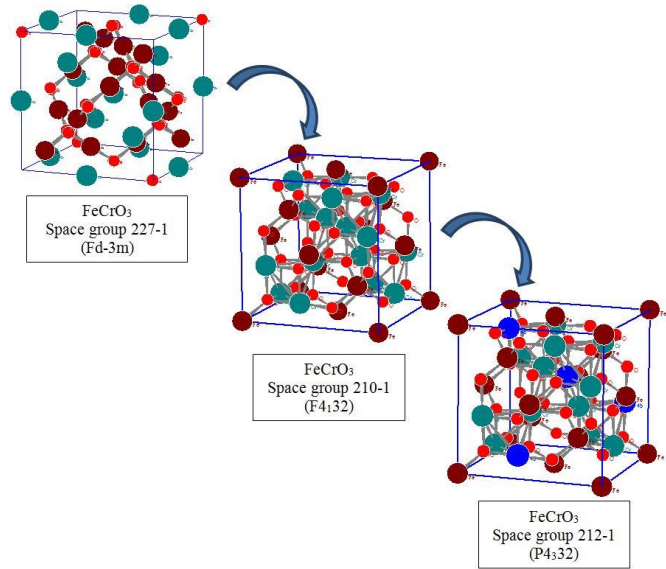


Figure 2. Models for EXAFS interpretation and vacancies occupation. Octahedral sites L1, L4, L7 and L10, shown in blue, are always occupied by either Cr^{3+} or Fe^{3+} .

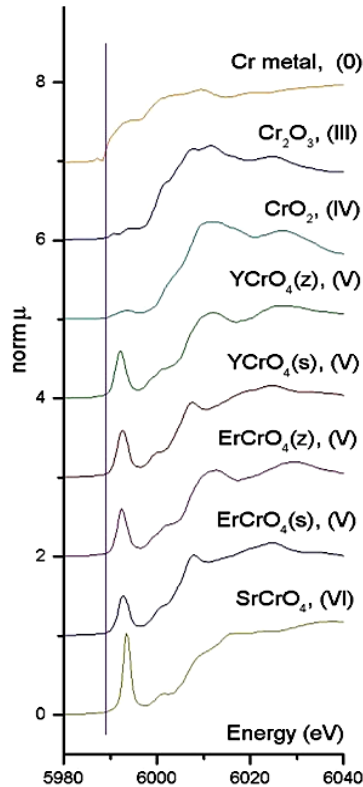


Figure 3. Comparison of Cr K-edge XANES spectra for different compounds. Increasing oxidation states are shown. First inflexion shifts to higher energies, as well as pre edge area rises, when increases the oxidation state.

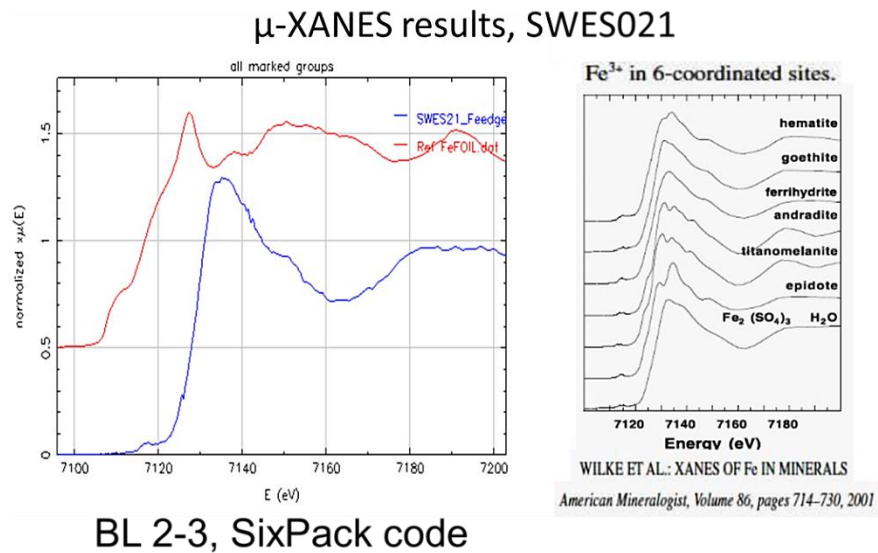


Figure 4. Comparison of Fe K-edge XANES spectra for the surface impurity of a selenite crystal with the iron standard. At right, XANES spectra of different minerals [5] presenting Fe^{3+} in 6-coordinated sites are shown, for identification of hematite impurities on the crystal surface.