



Experiment title: Unraveling the pre-edge nature of the Fe oxides absorption K edge by resonant inelastic x-ray scattering

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HE-1484

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ID-26

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Local contact(s):
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Report:

We report on the identification of the pre-edge structures at the Fe-K absorption edge in Fe-based minerals by resonant inelastic x-ray scattering (RIXS). In transition metal, the pre-edge region is usually ascribed to quadrupolar transition $1s \rightarrow 3d$ whereas the main absorption line results from dipolar transitions $1s \rightarrow p$. The fine structure of the pre-edge may serve as a signature of the site symmetry and valence of the transition metal atom. This is of prime interest particularly in Fe-based mineral, where Fe presents a rich variety of redox properties and chemical environment, and has led to numerous studies of the transition metal pre-edges by x-ray absorption spectroscopy (XAS) [1-2]. In fact, this description of the pre-edge features is correct if one assumes that i) the transition metal atom occupies a centrosymmetric site otherwise the pre-edge region has a mixed dipolar and quadrupolar character [3] ii) the d electrons can be treated as purely localized. In Fe-based mineral, none of these assumptions is fulfilled, since the Fe site is usually in a non-centrosymmetric site and hybridization of the d electrons with the surrounding ligand atoms cannot be precluded. To get a deeper insight into the pre-edge region and be able to discriminate between the various components XAS does not suffice any longer and finer spectroscopic probes of the transition metal electronic properties are required.

Resonant inelastic x-ray scattering is a powerful method of investigation of “hidden” excitations in the absorption edge. Because RIXS is a two-step process, schematically described by the successive absorption and emission of a photon, lifetime broadening effects related to the deep core hole in the XAS final state can be suppressed and information about the electronic properties of the atom under study can be obtained with an unprecedented resolution. In particular, quadrupolar excitation can be easily identified by RIXS, as shown in previous experiments [4]. Furthermore, the dispersion of the RIXS features with the incident energy provides information on the degree of localization or hybridization of the electronic states involved [5].

We have applied RIXS to a series of well-characterized Fe-based mineral samples. The experiment was carried out on the ID-26 beamline. The incident beam was monochromatized by a double crystal Si(220) monochromator and impinged on the samples, prepared in pellets, at 45°. The emitted x-rays at the Fe $K\alpha_{1,2}$ lines were analyzed using the IXS spectrometer installed on the ID-26 beamline. The spectrometer setup comprises a Si(333) spherically bent crystal as analyzer and a high-flux Peltier-cooled Si-diode detector laid down in the Rowland circle geometry, yielding at total energy resolution of 1.1 eV at 7 keV. Typical RIXS spectra, measured in andradite are shown on figure 1.

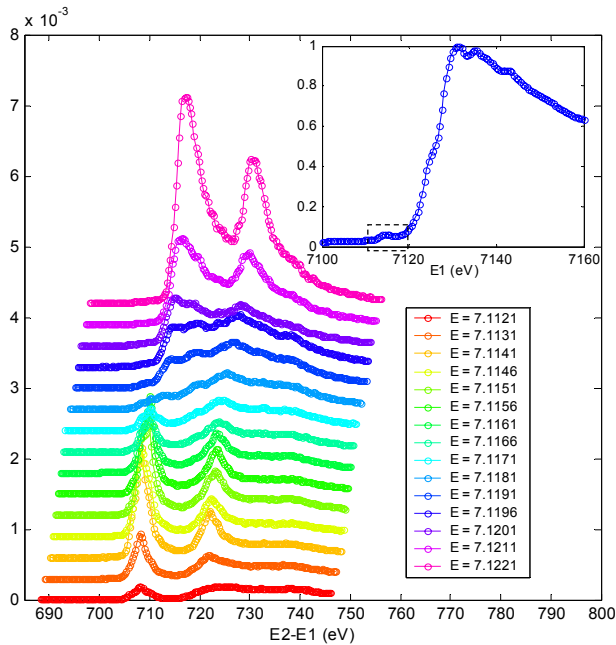


Figure 1 : set of RIXS spectra taken at different energies (in keV) in the Fe K pre-edge region of andradite. The XAS spectrum is shown in the inset and the region of interest indicated (dotted line).

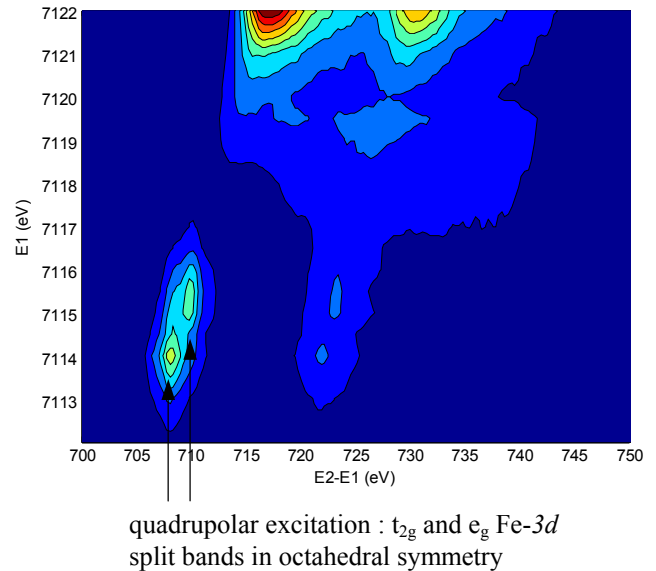


Figure 2 : Contour plot derived from the RIXS spectra. The quadrupolar states appear at constant transfer energy (E_2-E_1), as indicated by the arrows.

The spectra present a series of features appearing at constant transfer energy when the incident energy is tuned to the pre-edge region, which denotes the so-called Raman regime. The features, as clearly resolved on the contour plot in figure 2 on the lower left part, resonate at two different energies (7114 and 7115.5 eV). They can be tentatively assigned to the two $3d$ final states, in the presence of the $2p$ core hole, of Fe in octahedral symmetry, namely t_{2g} and e_g orbitals. At higher energy, one can observe a dispersion of the RIXS spectra linearly with E_1 indicating the uprising of the fluorescence regime, where dipolar transitions dominate (upper part of figure 2). In addition to andradite, RIXS was measured during the same run in siderite (Fe^{2+} in Oh symmetry) and in the non-centrosymmetric systems (Td site), staurolite (Fe^{2+}) and $LiAlO_2:Fe$ (Fe^{3+}), not shown here. In the later two, the different contour plot patterns and dispersions indicate the change of symmetry but also the importance of the $d-p$ hybridization already in the pre-edge region.

In a first step, the spectra will be analyzed by least square fitting in order to extract the quadrupolar and dipolar components and follow their evolution as function of incident energy. Simulations of the RIXS spectra within the multiplet approach as explained in Ref. [3] are also planned. Such analyses remain imperative for obtaining a detailed picture of the Fe electronic properties in these complex systems.

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