

INTERPRETATION OF Fe- XANES PRE-EDGE SPECTRA: PREDICTIONS BASED ON Co AND Fe OPTICAL SPECTRA.

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Introduction: Microanalysis of Fe³⁺/ΣFe in extraterrestrial samples at microscales comparable to that of an electron microprobe remains an important goal due to sample size constraints of upcoming sample return missions. Thus, work proceeds on technique development of the synchrotron micro-XANES technique. Specifically, we seek to understand causes of K edge features in Fe spectra, as explained by the “Z+1” model. Here we present a progress report on recent efforts, which focus on relating this theory of XANES spectroscopy, which predicts the multiplicity and energy of valence electron levels, with actual optical and XANES experimental spectra.

The Z+1 model for interpretation of Fe K edge transitions has been discussed by many workers [e.g., 1]. This model is based on the idea that when a 1s to 3d transition occurs, the resulting 1s hole is so close to the nucleus, that the outer orbitals see a configuration equivalent to that of the next highest ion on the periodic chart (i.e., Z+1). Thus, Fe K edge spectra can best be modeled by Co optical spectra. This model has been used successfully to understand the Fe K edge spectra of iron complexes [e.g., 2], that are sufficiently simple (relative to minerals) that ligand field theory and molecular orbital calculations give a good approximation of the allowable many-excited states. However, it has yet to be tested on minerals, because they are too complicated to be modeled. Co optical spectra are needed to provide an empirical link to Fe XANES results.

In this paper, we examine optical spectroscopy of Co in commonly-occurring minerals representing three different structure types. If the Z+1 model is valid, then these data provide the best approximations of the predicted peak energies in Fe XANES pre-edge spectra of those minerals. The Z+1 model is tested via comparisons between the Fe XANES and Co optical spectra of three sample minerals with increasingly distorted site symmetries: periclase, hematite, and garnet.

Background: Based on the Z+1 model, the unexcited energy levels of a Fe²⁺ cation normally assume a 3d⁶ configuration, but in a XANES experiment, the additional electron added to the 3d orbitals gives the ion a 3d⁷ configuration. So the XANES spectrum of Fe²⁺ is best approximated by the optical spectrum of Co²⁺, which also has a 3d⁷ configuration. Similarly, Fe XANES spectra of excited Fe³⁺ (3d⁶) are best understood by analogy with Co³⁺ (3d⁶) optical spectra.

The simplest Fe XANES pre-edge spectra to predict are therefore those for which Co optical spectra already exist and are well understood. For those minerals, direct calculation of Fe XANES pre-edge peak energies can be made using the appropriate Tanabe-Sugano diagram for each site in each mineral. Experimentally-derived values for crystal field splitting (Δ_O in crystal field theory and $10Dq$ in ligand field theory) and for the Racah B parameter can be used to predict the energies of each state. These can in turn be used to understand which peaks in the optical spectra of Co (or the XANES pre-edge spectra of the analogous valence state of Fe) correspond to which transitions.

Methods: Samples for study were selected from the collections of M.D.D. and G.R.R., along with supplemental samples from the Harvard Mineralogical Museum. Synchrotron micro-XANES (SmX) spectra were obtained using beam line x26a at the X-ray fluorescence microprobe facility, National Synchrotron Light Source (NSLS), Brookhaven National Laboratory and at the GeoSoilEnviroCARS beamline at the Advanced Photon Source, Argonne. Additional details are given in [3].

Results:

Periclase. The mineral species periclase (MgO) is made up of a cubic close-packed array of oxygen atoms with Mg²⁺ ions occupying octahedral sites. Each of these Mg sites has O_h point symmetry and is extremely symmetrical. The quadratic elongation of the sites is 1.0000, indicating the complete lack of distortion in the sites [4]. The observed pre-edge peak(s) in the Fe XANES spectra have, as predicted, low intensity. Optical spectra of Co²⁺ in the periclase structure already exist [5]. Three principal states are found in these Co²⁺ spectra: T_{1g}(⁴F) at 8,470 cm⁻¹ (1.05 eV), T_{2g}(⁴F) at 18,000 cm⁻¹ (2.23 eV), and T_{1g}(⁴P) at 19,600 cm⁻¹ (2.43) eV; $\Delta_O = 9,054$ cm⁻¹, or 1.12 eV. The latter two peaks would be too close to be resolved in a Fe XANES experiment because the natural line widths are ~1.3 eV, but the difference in energy between the lowest and two highest energy peaks should result in 3 peaks in the Fe XANES spectrum. The experimentally-observed Fe XANES spectrum of periclase is a weak, broad peak because the site is centrosymmetric; deconvolutions are in progress to try to fit this pre-edge to the 3 peaks predicted by the Co spectra and the Z+1 model.

