Interpretation of Fe K XANES Pre-Edge Spectra of Hematite Based on Cobalt Optical Spectra

S. R. Sutton,[1,2] M. D. Dyar,[3] J. S. Delaney,[4] M. Newville,[1] G. R. Rossman[5]
[1] GeoSoilEnviroCARS, and [2] Department of Geophysical Sciences, The University of Chicago, IL, UJ.S.A.
[3] Department of Earth and Environment, Mount Holyoke College, South Hadley, MA, U.S.A,.
[4] Department of Geological Sciences, Rutgers University, Camden, NJ, U.S.A.
[5] Diision of Geological and Planetary Science, California Institute of Technology, Pasadena, CA, U.S.A.

Introduction

Microanalysis of $Fe^{3+}/\Sigma Fe$ is an important goal in understanding the redox histories of terrestrial and extraterrestrial planetary materials. Our work explores the suitability of the synchrotron micro x-ray absosprtion near-edge structure (XANES) technique for this purpose. High-resolution XANES measurements have been reported on powders and glasses,[1,2] but proper interpretation of pre-edge peak multiplicity remains problematic. In this study, we tested the predictive capabilities of the "Z+1" model by comparing Fe K-XANES pre-edge spectra of hematite (corundum structure) with Co optical spectra of corundum. This approach would allow use of Co optical spectra to predict the multiplicity, orientational effects, and energy of valence electron levels in Fe XANES spectra of other important minerals.

Theoretical Approach

The Z+1 model for interpretation of Fe K-edge transitions has been discussed by many workers.[3] This model is based on the idea that when a 1*s* to 3*d* transition occurs, the resulting 1*s* 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). For example, the unexcited energy levels of a Fe^{2+} cation normally assume a $3d^6$ configuration, but in a XANES experiment, the additional electron added to the 3*d* orbitals gives the ion a $3d^7$ configuration. So the XANES spectrum of $_{26}Fe^{2+}$ is best approximated by the optical spectrum of $_{27}Co^{2+}$, which also has a $3d^7$ configuration. Similarly, Fe XANES spectra of excited Fe^{3+} ($3d^6$) are best understood by analogy with Co^{3+} ($3d^6$) optical spectra.

This model has been used successfully to understand the Fe K-edge spectra of iron complexes,[4] which 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, which are too complicated for theoretical models. Co optical spectra are needed to provide an empirical link to Fe XANES spectra. Effects of polarization on peak intensities (such as those characteristic of specific transitions in the optical spectra) should further facilitate assignment of peaks in similarly polarized XANES spectra to specific states.

We have surveyed the literature for optical spectroscopic studies of Co in commonly occurring minerals. 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. Here, the Z+1 model is tested via comparisons between the Fe XANES and Co optical spectra of hematite.

Table I. Crystal Field States in Corundum[8]

Cation	Final State	Energy (cm$_{-1}$)	Energy (eV)
Co^{3+}	$^1T_{1g}$	15,380	1.91
Co^{3+}	$^1T_{1g}$	15,740	1.95
Co^{3+}	$^3T_{2g}$	18,880	2.34
Co^{3+}	$^3T_{2g}/^3T_{1g}$	19,800	2.45
Co^{3+}	$^1T_{2g}$	22,800?	2.83
Co^{3+}	$^1T_{2g}$	23,170?	2.87
Co^{3+}	$^1T_{2g}$	30,000	3.72

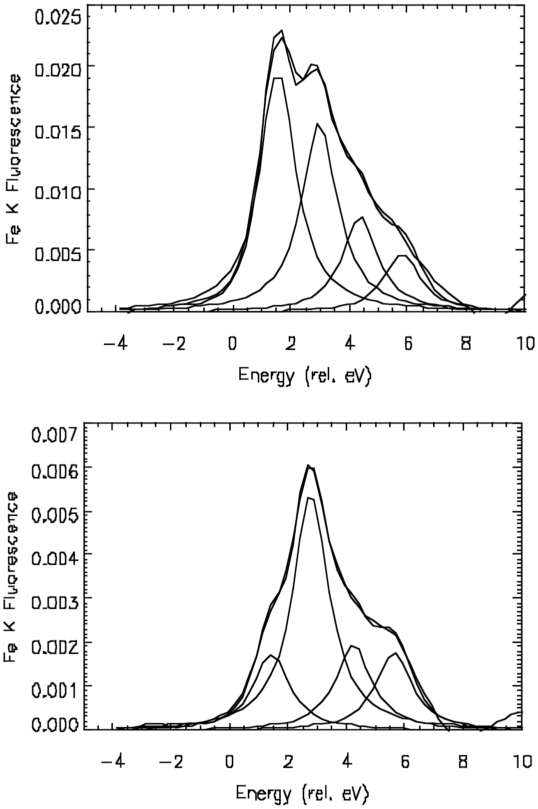

FIG. 1. Fe K pre-edge peak deconvolutions (after spline background subtraction) for hematite in two different orientations relative to the polarization plane. The four peaks predicted by Co^{3+} optical spectra (Table I) are observed in both spectra.

Experimental Method

Samples for this study were obtained from the Harvard Mineralogical Museum. Synchrotron micro-XANES (SmX) spectra[5,6] were obtained using the x-ray microprobe at the bending magnet beam line 13-BM-D (GeoSoilEnviroCARS). Kirkpatrick-Baez mirrors were used for focusing the 7 keV monochromatic beam, and fluorescence x-rays were detected with a Lytle chamber filled with argon.

Results

Hematite has a corundum structure, which consists of a hexagonal close-packed array of oxygen anions with trivalent cations occupying two-thirds of the octahedral interstices. Quadratic elongation of the site is 1.0200, which arises because the cation is off-center in the site. The cation occupying the site is Fe^{3+}, which is inherently noncentrosymmetric in XANES experiments. Optical spectra of Co^{3+} in synthetic corundum were reported.[7,8] The states are assigned as shown in Table I, and Δ_O for Co^{3+} is 17,410 cm^{-1} (2.16 eV). Four broad peaks should be resolved with the following relative energies: 0 (ground state), 1.9, 2.6 ± 0.3, and 3.7 eV.

Fe K-XANES pre-edge peaks are shown in Fig. 1 for hematite in two different crystallographic orientations relative to the polarization (horizontal) plane. As can be seen, all four peaks predicted by the optical analog model are observed. The results of Voigt fits to these peaks indicates relative peak energies of 0, 1.4, 2.8, and 4.2 eV. Thus, good agreement (within 0.5 eV) was obtained between the observed and predicted peak energies. Given the complexity of the optical transitions, this match between theory (Z+1 Co optical spectra) and experiment (Fe XANES spectra) is compelling. Further multiplet fits to these Fe XANES data are in progress to refine these results.

Acknowledgments

GeoSoilEnviroCARS is supported by NSF EAR-9906456 (M. Rivers, PI) and DOE DE-FG02-94ER14466 (S. Sutton, PI). Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38.

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