An Analytic X-Ray Absorption Near-Edge Spectroscopy Model for Compressed Fe_2O_3

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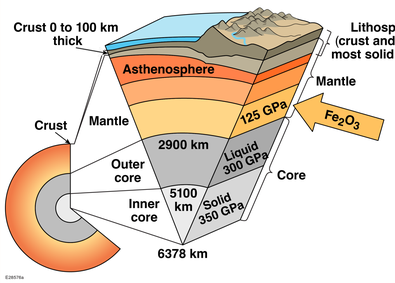
Abstract

Understanding various electronic and magnetic changes at high pressures in Fe_2O_3 is not only an important solid-state physics question, but is crucial in describing Earth's lower mantle. An x-ray absorption platform is being developed at the Laboratory for Laser Energetics to understand the electronic and crystal structure of compressed materials by simultaneously measuring x-ray absorption near, edge spectroscopy (XANES) and extended x-ray absorption fine structure (EXAFS). Fe_2O_3 was quasi-ramp compressed up to 700 GPa and the pressure was determined using a velocity interferometry system for any reflector (VISAR) on the OMEGA-60 laser. An analytic method to extract the electronic occupation and temperature of the compressed sample from the XANES edge is being developed and compared to electronic structure calculations from *ab initio* molecular-dynamics simulations based on density function theory. This material is based upon work supported by the Department of Energy National Nuclear Security Administration under Award Number DE-NA0003856.

Physical Motivation

Fe_2O_3 under extreme environments influences the evolution of the Earth and super-Earths

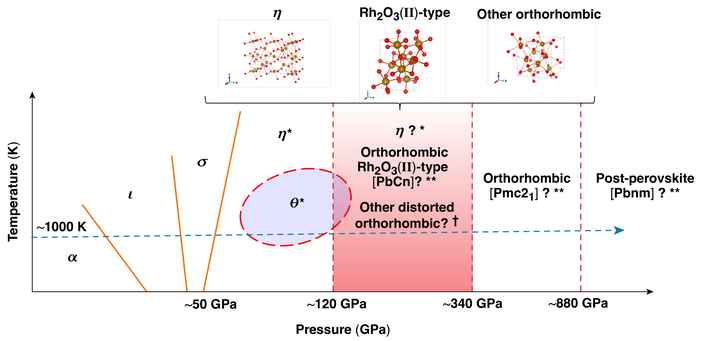


- Fe_2O_3 is a major component of banded iron formations (BIFs) which subduct ~1cm a year down to the core mantel boundary where increasing pressure causes decomposition producing 8-10 times more oxygen in the mantel than in the atmosphere.**
- This oxygen rich fluid in the deep earth's interior can significantly affect geochemical process by changing oxidation sates and mobilizing trace elements**

M. Williams, "What are the Earth's Layers?" Universe Today, Accessed 6 June 2022. https://phys.org/news/2015-12-earth-layers.html
*Q. Hu *et al.*, Nature 534, 241 (2016).
**E. Bykova *et al.*, Nat. Commun. 7, 10661 (2016).

The high-pressure behavior of Fe_2O_3 is still under debate, although theoretical and experimental studies suggest versatile structural, magnetic, and electronic properties

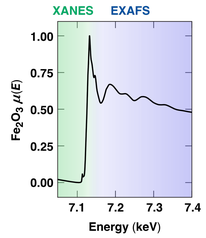
- The experimental capabilities of OMEGA permit pressures up to 700 GPa with temperatures 2000 to 5000 K
- These extreme conditions are challenging to produce at Earth's surface but are common throughout the universe



* E. Bykova *et al.*, Nat. Commun. 7, 10661 (2016).
** D.B. Ghosh and S. de Gironcoli, arXiv:0903.2104v1 (2009).
† USPEX structure searches

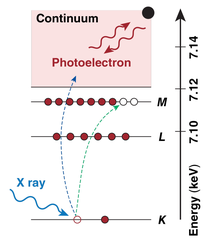
X-Ray Absorption Fine Structure (XAFS)

XANES and EXAFS spectroscopy can reveal the physical and electronic structure of materials at extreme conditions

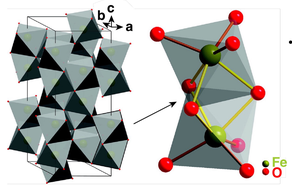


The photoelectron will interact with other atoms in the material

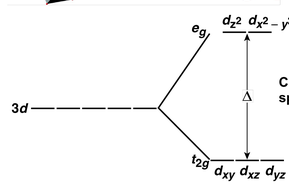
Bound–bound transitions generating features before the absorption edge

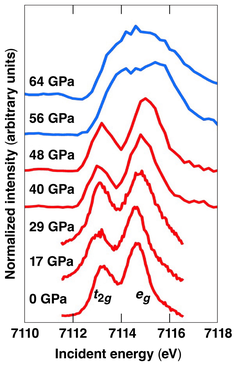


A pre-edge feature emerges upon compression of Fe_2O_3 to 700 GPa, significantly exceeding the pressure of other Fe_2O_3 XAFS measurements to date (~100 GPa)



- The pre-edge feature is due to a $1s \rightarrow 3d$ transition and is allowed under an electric dipole transition due to $3d, 2p$ orbital mixing or through the quadrupole transition*



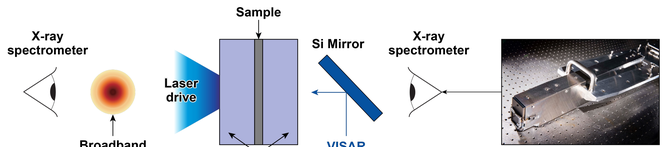


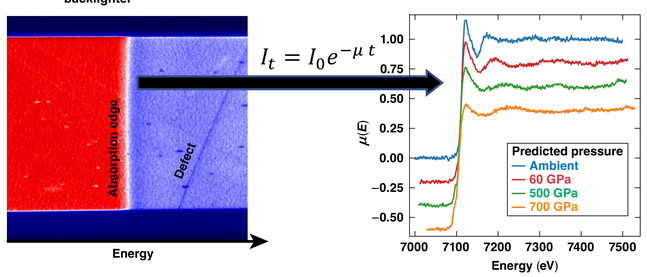
International X-Ray Absorption Socieyy: Fe_2O_3 Data, IXAS X-Ray Absorption Data Library. Accessed 6 June 2022. https://xaslib.xrayabsorption.org/elem/.

M. Newville, Rev. Mineral. Geochem. 78, 33 (2014).
K. Sivula *et al.*, J. Am. Chem. Soc. 132, 7436 (2010).
*S. Wang *et al.*, Phys. Rev. B 82, 144428 (2010).

Experimental Platform

We have developed a high-resolution x-ray spectrometer for XAFS experiments on OMEGA 60 at LLE



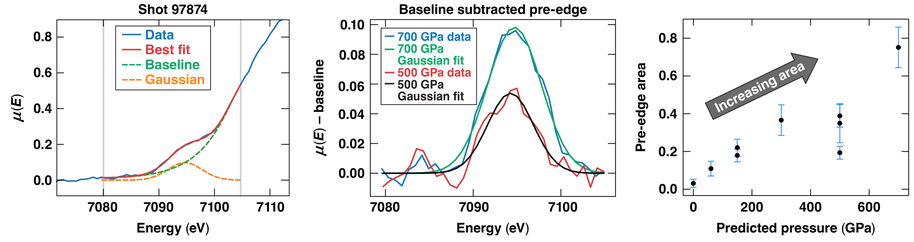


VISAR: velocity interferometry system for any reflector
D. A. Chin *et al.*, Phys. Plasmas 29, 052702 (2022).
Y. Ping *et al.* Phys. Rev. Lett. 111, 065501 (2013).

Pre-edge Analysis

The pre-edge was extracted and fit with a Gaussian whose intensity increased with pressure

$$f(x) = \underbrace{\frac{1}{\pi}\frac{\frac{1}{2}\Gamma}{(x-x_0)^2+\left(\frac{1}{2}\Gamma\right)^2} + a\,x + b}_{\text{Baseline}} + \underbrace{\frac{1}{\sigma\sqrt{2\pi}}e^{\frac{(x-\mu)^2}{2\sigma^2}}}_{\text{Gaussian}}$$

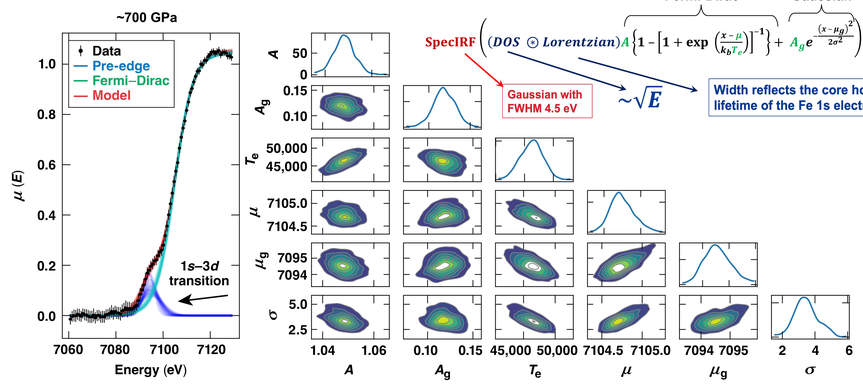


Pre-edge area increases with pressure could be because the system symmetry becomes increasingly disordered

M. Newville, J. Phys.: Conf. Ser. 430, 012007 (2013).

Analytical XANES Model

Bayesian analysis is used to constrain model parameters and their uncertainties

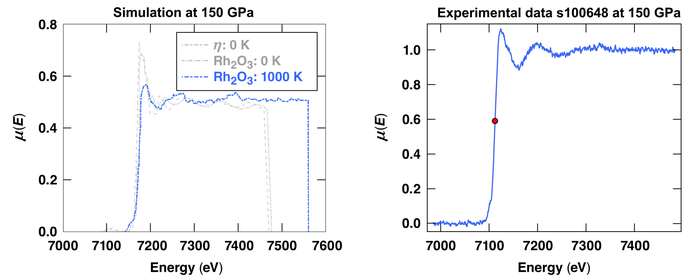


An analytical model of the edge is under development to determine the electron temperature and to approximate full DFT calculations in an effort to capture the essential physics of XANES.

J. Bradbury *et al.*, JAX: Composable Transformations of Python+NumPy Programs, Accessed 23 September 2022, https://github.com/google/jax.

Quantum Molecular-Dynamics DFT Simulations

DFT simulations are underway to predict XANES spectra which will be compared with data and analytical models



Simulations were calculated using QE + KGEC DFT.
Further convergence tests need to be run.