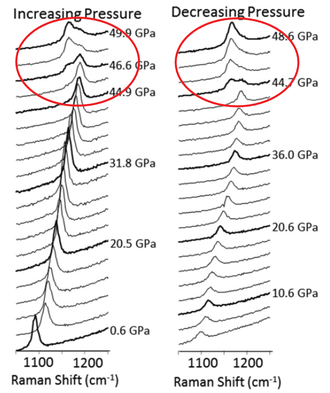
Bonding and Electronic Changes Associated with Spin Transition in Iron-containing Minerals

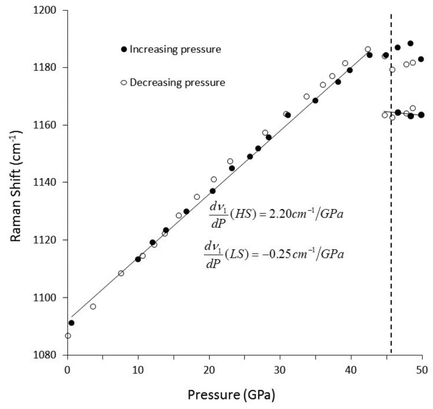
Shibing Wang*, Gabriela Farfan, Wendy L. Mao

Geological and Environmental Sciences, Stanford University; SIMES, SLAC Accelerator National Laboratory, * shibingw@stanford.edu

Spin transition is common with iron-containing minerals at the pressure condition of lower mantle. In this paper we present Raman spectroscopy study and x-ray absorption study of siderite and hematite respectively. For siderite, we observed the appearance of a new CO_3 symmetric stretching mode at 20 cm^{-1} lower frequency beginning at approximately 46 GPa. This softening is due to the lengthening of the C-O bonds as a result of a combination of rotation and volume shrinkage of the FeO_6 octahedra while siderite undergoes the isostructural volume collapse and spin transition. For hematite, the pressure-induced evolution of the electronic structure as Fe_2O_3 transforms from a high-spin insulator to a low-spin metal is reflected in the x-ray absorption pre-edge. The crystal-field splitting energy was found to increase monotonically with pressure up to 48 GPa, above which a series of phase transitions occur. Atomic multiplet, cluster diagonalization, and density-functional calculations were performed to simulate the pre-edge absorption spectra, showing good qualitative agreement with the measurements. The mechanism for the pressure-induced electronic phase transitions of Fe_2O_3 is discussed and it is shown that ligand hybridization significantly reduces the critical high-spin/low-spin transition pressure.

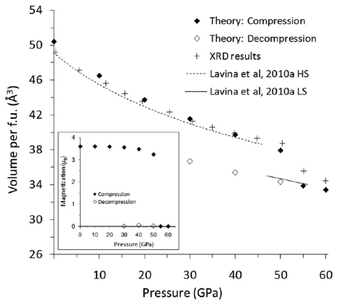
Bonding Change of Siderite ($FeCO_3$)

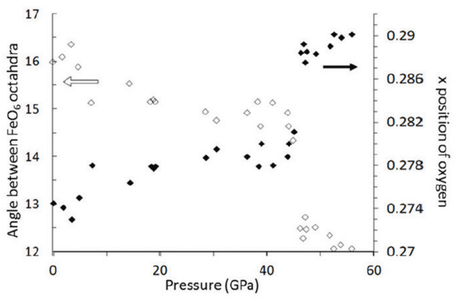


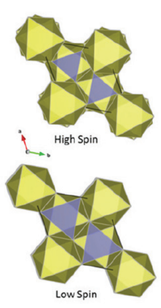


Left: Raman spectra of the v_1 peak in siderite under increasing and decreasing pressure. We see the frequency of the v_1 increase monotonically until a new, lower frequency peak emerges at approximately 46 GPa (outlined in red circles).

Right: Peak positions of the v_1 peak from the original Raman spectra, fitted with Peakfit. The dashed line shows where the new peak appears at ~46 GPa.





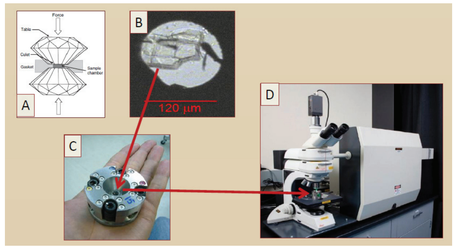


Up Left: XRD data (+) compared to our theoretical results (diamonds) and a previous study (lines). The red lines represent the range where the spin transition could occur in, based on these results. It is consistent with our Raman data.

Up Right: XRD data show that the angle between the FeO_6 octahedra correlates inversely with the x position of oxygen as pressure is increased (left). We have included an exaggerated diagram of how the structure changes with the spin transition. Notice how the FeO_6 octahedra (yellow) shrink and in turn stretch out the carbonate (blue triangles).

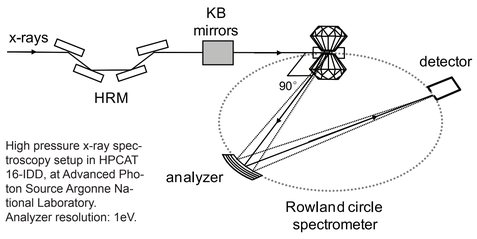
See for: G. Farfan, S. Wang, W.L.Mao, *et al*. Bonding and structural changes in siderite at high pressure, *American Mineralogist*, **91**, 1412 (2012)

Raman spectroscopy with Diamond Anvil Cell (DAC)

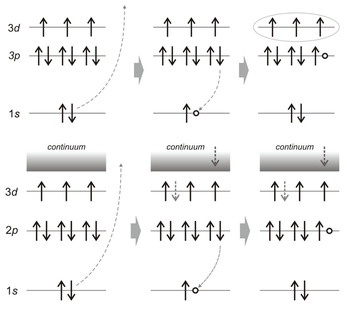


A. Schematic of DAC.
B. Siderite chip in a DAC.
C. A symmetric DAC.
D. Renishaw Raman Spectrometer at the Extreme Environments Laboratory, Stanford University

X-ray Spectroscopy with Diamond Anvil Cell (DAC)



High pressure x-ray spectroscopy setup in HPCAT 16-IDD, at Advanced Photon Source Argonne National Laboratory. Analyzer resolution: 1eV.



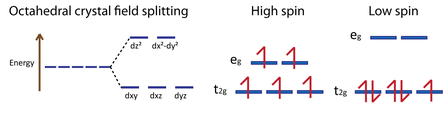
Schematics of x-ray K-edge absorption

Schematics of x-ray Kβ emission.

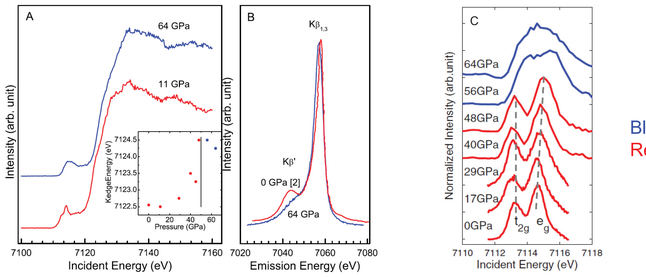
Spin Transition of Hematite (Fe_2O_3)

Properties of Fe_2O_3 at ambient and high pressure		
	Ambient Conditions	High Pressure (>40-60 GPa)
Crystal Structure	Al_2O_3 Hexagonal	Rh_2O_3-II Orthorhombic
Electronic Property	Insulator	Metal
Magnetic Moment	High-spin	Low-spin

Fe_2O_3 powder is loaded into a panoramic DAC with Be gasket, with He or Ne as pressure transmitting medium.

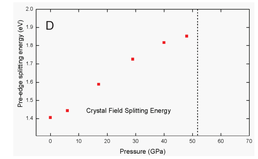


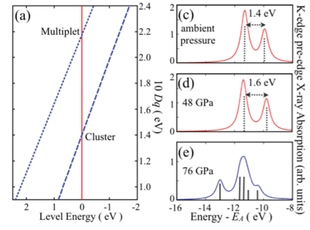
Crystal Field Splitting of Fe^{3+} in a octahedral geometry, and the high-spin (HS) and low-spin (LS) electron configuration.



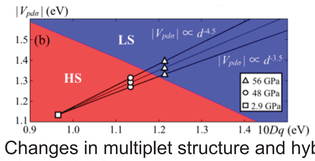
Blud: LS
Red: HS

A. X-ray K-edge absorption of Fe_2O_3 at different pressure.
B. X-ray Kβ emission of Fe_2O_3 at different pressure.
C. Pre-edge of absorption spectra
D. Fitted crystal field splitting energy increases from 1.4 eV to 1.85 eV at 48 GPa, right before the transition pressure.





(a): Energy of LS state for the single atom multiplet calculation (dotted line) compared with the FeO_6 cluster diagonalization (dashed line) relative to the HS state solid line.
(c)(d)(e): K-edge pre-edge XAS spectra from the FeO_6 cluster calculation at various pressures; E_A is the Fe K-edge absorption energy.



(b): HS-LS phase diagram for Fe_2O_3. The dotted line shows the probable trajectory of 10Dq,Vpd with increasing pressure.

Changes in multiplet structure and hybridization are important for a quantitative estimate of the HS-LS transition pressure. Local cluster physics gives excellent agreement between the observed pressure dependence of the experimental and calculated spectra.

See for: S. Wang, W.L.Mao, *et al*. High-pressure evolution of Fe_2O_3 electronic structure revealed by x-ray absorption, *Physical Review B* **82** 144428 (2010)