High pressure evolution of Fe_2O_3 electronic structure revealed by X-ray absorption

Shibing Wang,[1,2] Wendy L. Mao,[2,3,4] Adam P. Sorini,[2] Cheng-Chien Chen,[2,5] Thomas P. Devereaux,[2,6] Yang Ding,[7] Yuming Xiao,[8] Paul Chow,[8] Nozomu Hiraoka,[9] Hirofumi Ishii,[9] Yong Q. Cai,[10] and Chi-Chang Kao[11]

[1]*Department of Applied Physics, Stanford University, Stanford, California 94305, USA*
[2]*SIMES, SLAC National Accelerator Laboratory, Menlo Park, California 94025, USA**
[3]*Photon Science, SLAC National Accelerator Laboratory, Menlo Park, California 94025, USA*
[4]*Department of Geological and Environmental Sciences,*
Stanford University, Stanford, California 94305, USA
[5]*Department of Physics, Stanford University, Stanford, California 94305, USA*
[6]*Geballe Laboratory for Advanced Materials, Stanford University, Stanford, California 94305, USA*
[7]*HPSynC, Carnegie Institution of Washington, Washington, DC 20015, USA*
[8]*HPCAT, Carnegie Institution of Washington, Washington, DC 20015, USA*
[9]*National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan*
[10]*NSLS-II, Brookhaven National Laboratory, Upton, New York 11973, USA*
[11]*NSLS, Brookhaven National Laboratory, Upton, New York 11973, USA*
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We report the first high pressure measurement of the Fe K-edge in hematite (Fe_2O_3) by X-ray absorption spectroscopy in partial fluorescence yield geometry. 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 phase transitions of Fe_2O_3 is discussed and it is shown that ligand hybridization significantly reduces the critical high-spin/low-spin gap pressure.

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An archetypal $3d$ transition metal oxide and important geological compound, α-Fe_2O_3 (hematite) undergoes a series of structural and electronic transitions at high pressure. At ambient conditions, Fe_2O_3 is an antiferromagnetic insulator, and adopts the corundum structure. This structure is maintained until approximately 50 GPa whereupon it transforms to a Rh_2O_3(II)-type structure [1], accompanied by a 10% drop in volume. The structural transition are associated with changes in magnetic and electronic structure. X-ray K_β emission at ambient pressure and 72 GPa show that the magnetic moment drops from high-spin (HS) to low-spin (LS) at high pressure [2]. Conductivity measurements indicate that an insulator to metal transition occurs between $40-60$ GPa [3].

The nature of these transitions has been a popular research topic over the past decade. Based on their structural study of the Rh_2O_3-II phase, Rozenberg *et al.* have suggested that the charge-transfer gap closure is responsible for metallization and concurrent spin moment transition [1]. Combined local density approximation and dynamical mean-field theory calculations by Kuneš *et al.* have implied that the reduction of the Mott gap with pressure drives the volume collapse and structure change [4]. This idea appears to be at odds with experimental observations of a metastable state in which the LS and corundum structure occur simultaneously [5]. Thus, despite many studies of the transitions in Fe_2O_3,

the nature of the evolution of the electronic structure with pressure remains unresolved.

A number of spectroscopic techniques have been applied to investigate the electronic configuration of $3d$ transition metal compounds. Photoemission and x-ray L-edge absorption provide useful information on the 3d-levels of transition metals, but unfortunately, these probes cannot penetrate the high pressure cells. X-ray absorption spectroscopy (XAS) at the K-edge of $3d$ transition elements, however, operates in the hard x-ray regime, allowing the study of the electronic structure at high pressure.

The pre-edge region of the K-edge absorption spectrum can be used to investigate 3d-electrons of transition metal compounds. In Fe-bearing compounds, the pre-edge spectra contain information about the oxidation state and local coordination [6]. However, limited by the $1s$ core-hole lifetime broadening, the energy resolution using a transmission geometry is not sufficient to resolve the detailed structure of the pre-edge region. Therefore we use the partial fluorescence yield method for measuring absorption. Instead of collecting the transmitted x-ray, the $K_{\alpha1}$ emission line is measured. This method thus has a $2p$ core hole lifetime broadening of about 0.3 eV, resulting in much higher energy resolution.

Here we present the first high pressure XAS measurement in partial fluorescence yield on Fe_2O_3 up to 64 GPa. The improved resolution of the resulting spectra shows
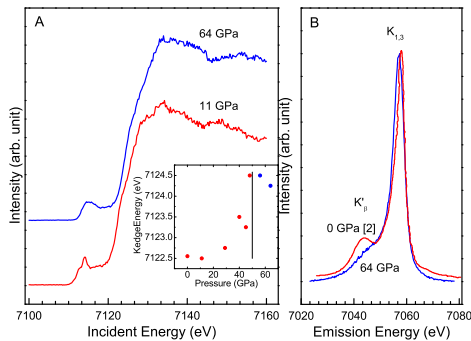
FIG. 1: (color online). A: X-ray K-edge absorption spectra of Fe_2O_3 in partial fluorescence yield geometry at 11 GPa and 64 GPa; Inset: Fe K-edge position at different pressures. The edge is determined by the maximum of the first derivative of the absorption spectra. B: X-ray K_β emission spectra of Fe_2O_3 at 64 GPa and 0 GPa from Ref. 2, showing the reduction of the spin moment. Red: high spin state; blue: low spin state.
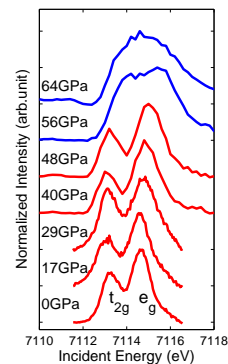

FIG. 2: (color online). X-ray K-edge pre-edge of Fe_2O_3 at 0, 17, 29, 40, 48, 56 and 64 GPa. The bottom 3 spectra are from SPring-8 using high resolution monochromator, and the top 4 spectra are from APS using diamond monochromator.

Pressure (GPa)	0	6	17	29	40	48
CFSE (eV)	1.41	1.44	1.59	1.73	1.82	1.85

TABLE I: Crystal field splitting energy (CFSE) of Fe_2O_3 as a function of pressure.

the evolution of the Fe^{3+} $3d$ electronic structure as the material undergoes its complex pressure-induced transitions. Previously, Caliebe *et al.* applied this technique to Fe_2O_3, and assigned the double-peak structure of the pre-edge to the t_{2g} and e_g components of the $3d$ band [7] as suggested [8] previously. Similar methods have been used to study orbital hybridization and spin polarization of Fe_2O_3 [10] and pre-edges of other Fe-containing compounds [11].

Fe_2O_3 powder was loaded in a hydrostatic pressure transmitting medium (He or Ne) in an X-ray transparent Be gasket. Ruby fluorescence was used for pressure calibration. High pressure XAS spectra of Fe_2O_3 were collected at two 3rd generation synchrotron facilities. In both setups, monochromatic X-rays focused by Kirkpatrick-Baez mirrors were directed through a panoramic diamond anvil cell, and the analyzer was fixed at 90° from the incident beam.

In the SPring-8 XAS experiment conducted at BL12XU, we scanned the incident x-ray energy from 7110 to 7145 eV with a step size of 0.1 eV and over the smaller range of 7112 to 7115 eV at 0.05 eV step size. In the APS setup at HPCAT 16-IDD, the entire edge was scanned from 7100 to 7160 eV with a step size of 0.25 eV. The pre-edge was scanned from 7108 to 7118 eV (7109 to 7119 eV for 56 and 64 GPa) with a step size of 0.2 eV. For both measurements, the partial fluorescence yield was collected with the analyzers set at the Fe $K_{\alpha1}$ energy (6405.6 eV).

Figure 1A shows the representative Fe K-edge XAS spectra for Fe_2O_3. The partial fluorescence yield geometry allows us to resolve the pre-edge features. At the highest pressure in our study, we collected the K_β emission spectrum of the sample shown in Figure 1B. Com-

pared with the 0 GPa spectrum of Badro *et al.*, there is a dramatic reduction in the K_{β}' satellite peak intensity in the 64 GPa spectrum, indicating a LS ground state [2, 9].

As shown in Figure 1A inset, it is also observed that the K-edge blue shifts with pressure until the phase transition region, and remain approximately constant thereafter. This shift of K-edge with pressure is also observed in other $3d$ transition metal oxides [12], a result of the increase of electron density upon compression.

Figure 2 shows the Fe K-edge pre-edge spectra of the sample from ambient pressure to 64 GPa. The pre-edge features at ambient pressure are associated with excitations to t_{2g} and e_g orbitals, split by the octahedral crystal field. Our ambient pressure data can be fit with a crystal field splitting energy (CFSE) of 1.4 eV, consistent with previous observation [7, 8]. The two-peak feature in the pre-edge persists until 48 GPa, just before the phase transitions occur. By fitting the pre-edge spectra we estimate a monotonic increase of the CFSE to 1.85 eV at 48 GPa, as shown in Table I. This increase is expected as the FeO_6 octahedra shrink with pressure, and the shorter metal-ligand distance elevates the e_g level relative to the t_{2g} level.

The pre-edge spectra above the phase transitions (*i.e.* above 48 GPa) are more complicated to interpret. The FWHM of the pre-edge features significantly broadens and a simple assignment in terms of single particle t_{2g} and e_g transitions is inconsistent; at such pressures, Fe_2O_3 is in the LS state in which e_g should be empty and five of the six t_{2g} states occupied. Such a single particle con-
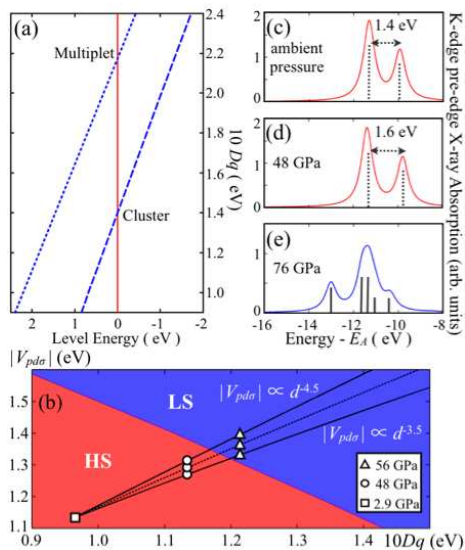
FIG. 3: (color online). (a) Energy of LS state for the single atom multiplet calculation (dotted line) compared with the FeO_6 cluster diagonalization (dashed line) relative to the HS state (solid line). (b) HS-LS Phase diagram for Fe_2O_3. The dotted line shows the probable trajectory of $(10Dq, V_{pd\sigma})$ with increasing pressure (see text). (c)-(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. At ambient pressure (c), the spectrum shows distinct t_{2g}-e_g absorption peaks separated by 1.4 eV, indicating a high-spin ground state. At 48 GPa (d), the peak separation is 1.6 eV, and the ground state still resides in the high-spin sector. At 76 GPa (e), the spectrum shows broad, multiple peaks, indicating a low-spin ground state. All the spectra were broadened with a 0.3 eV Lorentzian.

figuration should lead to relatively small (large) t_{2g} (e_g) amplitudes, unlike the features observed in the pre-edge spectra at 56 and 64 GPa.

To understand the pressure dependence of the XAS, we first used crystal-field atomic multiplet theory to calculate the electronic structure. The relevant parameters are the atomic t_{2g}-e_g energy level spacing $10Dq$ [13], and the "Racah parameters" B and C associated with d-d interactions [14]. We fix Racah $B = 0.075$eV and $C = 0.346$eV appropriate for solid-state Fe^{3+} systems [15], and perform calculations for a range of $10Dq$. The lowest two eigenenergies for the $(1s)^2(3d)^5$ configuration are shown in Fig. 3(a) from which a HS-LS transition is evident near $10Dq = 2.2$eV. For low pressure (low Dq) the ground state has $^6A_1$ character (HS) and crosses over at high pressure to a state of $^2T_2$ character (LS) [16].

While the critical value of $10Dq$ determined by the atomic multiplet calculation is larger than that suggested by the experimental t_{2g}-e_g peak splitting in Fig. 2, it is well-known that the critical $10Dq$ for the HS-LS transition is reduced by the Fe-O charge-transfer processes. We perform calculations on a FeO_6 octahedral cluster that explicitly includes multiplets, ligand hybridization

and charge-transfer via the Slater-Koster matrix elements [18], Racah parameter A, and charge-transfer gap energy Δ. At ambient pressure, the values of the parameters are (in units of eV): $V_{pd\sigma} = -1.13$, $V_{pd\pi} = 0.65$, $V_{pp\sigma} = 0.56$, and $V_{pp\pi} = -0.16$, $A = 5.0$, $10Dq = 0.96$, and $\Delta = 2.7$ [18]. We have used the smaller value of $V_{pd\sigma}$ from Ref. 18. The lowering of the critical $10Dq$ is illustrated in Fig. 3(a), which shows the energies of the HS and LS states calculated in the FeO_6 cluster compared to atomic multiplet theory as a function of $10Dq$. The HS to LS transition occurs at smaller $10Dq$ since the hybridization most strongly couples the d^5 LS state with the $d^6\underline{L}$ LS state, lying lower in energy than the $d^6\underline{L}$ HS state.

These parameters yield the ambient pressure spectra shown in Fig. 3(c), which is in good agreement with experiment (cf. Fig. 2 and Table I). The two spectral peaks separated by ~ 1.4 eV correspond to excitations into the t_{2g} and e_g orbitals respectively and indicate a HS ground state, with the observed CFSE coming from $10Dq$ plus a 0.45 eV covalent contribution. Thus while the critical $10Dq$ is reduced by the Fe-O charge transfer processes, the ligand field splitting due to covalency pushes up the spectral t_{2g}-e_g peak separation of the XAS spectra [7].

With parameters set to reproduce ambient spectra, we consider the pressure evolution of the HS-LS transition and the XAS spectra. As the pressure increases, both $10Dq$ and the hopping integrals increase, respectively having $\sim d^{-5}$ and $\sim d^{-4}$ Fe-O bond length dependence [13, 18]. The combined effect of pressure-dependent hopping and $10Dq$ is explained in the phase diagram of Fig. 3(b). We consider several variations of $V_{pd\sigma}$ with d as shown in Fig. 3(b), which all indicate that the critical pressure occurs between 52 and 55 GPa. Although variation of the exponent of $V_{pd\sigma}$ induces a variation on the order of 5% in the predicted critical pressure it is striking to observe that the experimentally observed limits on the critical pressure are in general agreement with theoretical predictions.

Figures 3(c)-(e) show the calculated pre-edge XAS spectra from the FeO_6 cluster at various pressures. The spectrum at 48 GPa (Figure 3(d)) shows a clear two peak structure in the HS state, with a t_{2g}-e_g peak separation of $\sim$1.6 eV. The calculated CFSE is $\sim 15\%$ smaller in energy than experiment, which may be in part due to structural deviations from octahedral symmetry giving inequivalent Fe-O bonds not included in the cluster calculation [1], as well as the overall uncertainty in cluster parameters. Figure 3(e) shows the calculated XAS spectra at 76 GPa. The high pressure spectra has multiple-peak features indicating a LS ground state; this qualitative change in character of the ground state is reflected as a qualitative change in the calculated spectra. It is the simple transformation properties (A_1) of the HS state that allow the XAS to be interpreted in terms of single particle t_{2g} and e_g levels; the final state, with one addi-
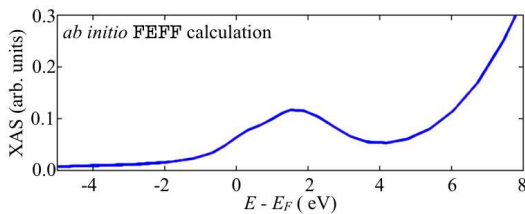
FIG. 4: *ab initio* calculations with the `FEFF` software of the pre-edge region of the Fe K-edge XAS spectra for the high pressure metallic $Rh_2O_3(II)$-type structure of Fe_2O_3. E_F is the fermi level.

tional d-electron, transforms as $A_1 \otimes (T_2 \oplus E) = T_2 \oplus E$ mimicking the single particle t_{2g} and e_g levels. On the other hand, addition of a d-electron to the LS state yields $T_2 \otimes (T_2 \oplus E) = A_1 \oplus E \oplus T_1 \oplus T_2 \oplus T_1 \oplus T_2$ resulting in more peaks than would be expected based on a single particle interpretation.

While an insulator-metal transition is not necessarily concomitant with a change in the local spin configuration (and *vice versa*), a low spin metallic state is always expected at a high enough pressure. In this regime, we use the all-electron `FEFF` code [23] to calculate the high pressure Fe K-edge XAS for a large cluster of atoms in the high pressure structure. Figure 4 shows the calculated pre-edge XAS, having broad pre-edge features in qualitative agreement with the experiment at and above 56GPa.

We last turn to the electronic phase transition mechanism. Badro *et al.* have shown the coexistance of LS and corundum structure indicating that the electronic transition can not drive the structural transition. Kunes *el al.* divided the electronic transition into a Mott gap closing and a HS-LS gap closing, and estimated the respective regimes of stability via a local "density-based interaction". Here we have indicated the importance of atomic multiplets and ligand hybridization. Our results indicate the location of the HS-LS transition can be well-described within the charge-transfer multiplet-hybridization cluster approach and reasonable choices for the pressure-dependence of the cluster parameters. The reduction of the critical pressure for the HS-LS transition in comparison with atomic multiplet theory due to ligand hybdrization is seen to be significant. These results lead to the prediction that the critical pressure occurs between 52 and 55 GPa, at values of $10Dq$ much smaller than would be expected from atomic multiplet theory based on the experimental spectra. While our cluster calculation cannot address in detail the closing of a bulk Mott gap, the observed reduction of the HS-LS transition pressure leads us to suggest that the physics of a local HS-LS transition should be strongly reconsidered as the key ingredient giving the evolution of spectral features observed in the pre-edge XAS spectra with pressure.

In summary, we measured x-ray absorption spectra of Fe_2O_3 up to 64 GPa, and for the first time experimentally resolved the crystal field splitting and its pressure dependence through the metal-insulator transition. The CFSE increases from 1.41 eV at ambient conditions to 1.85 eV at 48 GPa. The pre-edge features change drastically at higher pressures corresponding to the range where a number of electronic and structural transitions have been reported. We constructed the phase diagram for Fe_2O_3 which shows that the changes in multiplet structure and hybridization are important for a quantitative estimate of the critical pressure. Based on considerations of local cluster physics, excellent agreement between the observed pressure-dependence of the experimental and calculated spectra were obtained.

* Corresponding author: shibingw@stanford.edu
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generic features.

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