***Graphical Abstract (for review)**

Fe_3O_4

Fe L-edge XAS

Determination of the Surface Electronic Structure of Fe₃O₄(111) by Soft X-ray Spectroscopy

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Abstract

The determination of surface terminations in transition metal oxides is not trivial because many structural configurations could be possible. They exhibit various terminations depending on the oxidation states of metal cations exposed to the surface. Fe₃O₄ is one example in which octahedrally and tetrahedrally coordinated Fe²⁺ and Fe³⁺ cations coexists with oxygen anions. For the identification of the surface termination of Fe₃O₄(111) grown on Pt(111) we have employed surface sensitive synchrotron based X-ray photoelectron and absorption spectroscopy. It has been shown that the topmost surface is octahedrally coordinated Fe³⁺ rich.

Keywords: Fe₃O₄, magnetite, Fe₂O₃, hematite, thin film, XPS, XAS, O K-edge, Fe L-edge, surface sensitivity

1. Introduction

The surfaces of iron oxide compounds have been the focus of much interest because of their chemical and electronic properties, which are significantly different from those in their bulk state [1]. Among iron oxides, Fe₃O₄ (magnetite) has been in particular studied, due to their importance in catalysis, in environmental chemistry as an active agent, in corrosion science and also due to their magnetic/electronic properties [2].

Fe₃O₄ has the inverse spinel structure where Fe³⁺ cations occupy a quarter of the tetrahedral A sites (Fe_{tet}) and Fe³⁺ and Fe²⁺ cations occupy half of the octahedral B sites (Fe_{oct}). Fe₂O₃ (hematite) on the other hand has a corundum structure, Fe³⁺ double layers occupy 2/3 of the octahedral sites (Fe_{oct}) and oxygen anions complete hexagonal lattice in a distorted fashion [1]. Fe₃O₄ has been investigated heavily in the forms of natural single crystals and crystalline thin films grown on metals and oxide substrates [2]. Despite intense research, contradicting atomic arrangements terminating Fe₃O₄(111) surfaces have been proposed due to its reactive nature and sensitivity to the preparation conditions.

Theoretically, there are in total six different possible surface terminations along the [111] direction of a Fe_3O_4 crystal; among two of which have commonly been proposed to be the most stable ones. Initially $1/4$ ML of Fe, in other words the $\text{Fe}_{\text{tet}}\text{-O-Fe}_{\text{oct}}\text{-O}$ [3–5], has been suggested as the terminating layer in ultra-high vacuum (UHV) conditions, but later on thermal desorption and infrared spectroscopy studies of adsorbed CO have indicated that $1/2$ ML Fe terminations, $\text{Fe}_{\text{oct}}\text{-Fe}_{\text{tet}}\text{-O-Fe}_{\text{oct}}\text{-O}$, were more likely the case [6,7]. Larger molecules that can coordinate more than one adsorption site potentially give additional information. The conclusions of a scanning tunneling microscopy (STM) study of adsorbed formic acid, pyridine, and carbon tetrachloride points out the importance multiple possible surface terminations and possibility of abundant Fe_{tet} sites on the surface [8]. A more recent STM supports the finding that the Fe_{tet} sites are more commonly observed, Fe_{oct} termination is more likely to form if they are annealed in oxygen poor environments [4]. Oxygen terminated surfaces have also been shown to exist as the samples are cooled down in oxygen ambient after annealing [9]. The variations in these observations are related to the oxygen partial pressure dependence and annealing temperatures in the preparation steps. For instance, $\text{FeO}_x(111)$ -like surface terminations have been reported as the samples were annealed at 870 K in 10^{-6} Torr oxygen ambient [10,11]. It has also been shown that $\text{FeO}_x(111)$ -like reduced surface patches and regular surface regions can coexist on natural single crystals [12]. DFT calculations [13] predict that the surface structures discussed above are stable within a broad oxygen chemical potential regime and within several other possible terminations, unreconstructed $\text{Fe}_{\text{oct}}\text{-Fe}_{\text{tet}}\text{-O}$ surface has been found to be the most stable one.

X-ray photoelectron spectroscopy (XPS) is commonly used for surface compositional analysis and electronic structure determination [14]. Utilization of synchrotron radiation sources with tunable photon energy makes extremely surface sensitive measurements possible. Since the probing depth depends on the mean free paths of the photoelectrons, enhanced surface sensitivity could be achieved by setting the electron kinetic energies to 100-150 eV regime. Further surface enhancements could be obtained by changing the electron detection angles with respect to the electron spectrometers. Electrons emitted from the surfaces at grazing angles make probing only first two atomic layers possible.

X-ray absorption spectroscopy (XAS) is on the other hand a powerful method for identifying the electronic structures of iron oxides because of the orbital symmetry selectivity. In the absorption process, photons at specific energies excite a core electron to an empty state above the Fermi level. Since the excitation processes are governed by the dipole selection rules; local bonding geometries could be probed thanks to polarized synchrotron light. Thus the O K-edge and Fe L-edge XAS spectral analysis provide information about the oxidation state and the symmetry of the O and Fe ions. O K-edge absorption spectrum reflects the dipole allowed transitions mainly to the O 2p states [15]. The L-edge X-ray absorption spectrum is dominated by dipole-allowed transitions to Fe 3d and 4s final states. Because of much larger wave function overlap with the d orbitals the excitation cross-section with the s orbitals is usually ignored. XAS

is however a bulk sensitive method due to the nature of the electron yield or fluorescence yield measurement methods [16].

Even though total or Auger electron yield methods are based on electron detection, higher kinetic energies (for Auger electron yield methods) and contributing secondary electrons make XAS measurements less surface sensitive compared to the sensitivity of XPS. For example, kinetic energy of oxygen KVV Auger decay electrons is around 500 eV, which is probing approximately 1 nm surface depth. Similarly, further surface enhancements could be obtained if the Auger electrons emitted from the surfaces are recorded at grazing angles. The details of the XPS and XAS measurements are given in Materials and Methods section below.

Bulk electronic and magnetic structures of Fe_3O_4 and Fe_2O_3 have been investigated by XPS and XAS (and also by electron energy loss spectroscopy), many studies on the interpretation of O K-edge and Fe L-edge XAS spectra have been reported [15,17–21]. Although there are few surface sensitive XPS measurements [22], so far no systematic XAS investigations on the local coordination and electronic structures of the surface atoms terminating iron oxide single crystal surfaces have been performed.

Here, we present surface and bulk sensitive XPS and XAS experiments of $\text{Fe}_3\text{O}_4(111)$ thin films grown on Pt(111). Depending on the preparation methods high quality stoichiometric $\text{Fe}_3\text{O}_4(111)$ films as well as more $\alpha\text{-Fe}_2\text{O}_3$ like films could be generated. The results of surface sensitive XPS, O K-edge and Fe L-edge XAS spectra indicate that the local coordination of Fe cations at the topmost surface of $\text{Fe}_3\text{O}_4(111)$ films could be similar to the octahedral Fe^{3+} coordination in Fe_2O_3 .

2. Material and methods

The experiments were performed at the elliptically polarized undulator (EPU) beamline 13-2 at Stanford Synchrotron Radiation Lightsource (SSRL). The ultra-high vacuum (UHV) end-station with a base pressure better than 2×10^{-10} Torr is equipped with an electron energy spectrometer (Scienta R3000), high throughput slit-less home-made X-ray emission spectrometer, low energy electron diffraction (LEED) optics (SPECS), e-beam evaporator (EFM 3, Omicron), and standard tools for sample cleaning.

Pt(111) single crystal, $\text{Fe}_3\text{O}_4(111)$ and $\text{Fe}_2\text{O}_3(0001)$ were used as a substrate and as thin film iron oxide samples, respectively. Pt(111) single crystal was cleaned by repeated cycles of Ne^+ ion bombardment and annealing to 1250 K. Segregated carbon impurities were burned off by exposing the surface to O_2 while cooling down (from 800 K to 400 K). Long range order and surface cleanness were confirmed by the hexagonal (1×1) sharp LEED patterns and XPS, respectively. Sample heating was performed by a standard electron bombardment method, by accelerating electrons emitted from a hot filament placed backside of the sample. Temperature was measured by a K-type thermocouple spot-welded onto the side of the sample. Oxygen gas was dosed into the system by a variable leak valve.

Fe₃O₄(111) films were grown on Pt(111) surface by repeated cycles of physical vapor deposition of iron and post oxidation at elevated temperatures. The details of the film preparations can be found elsewhere [23,24]. Briefly, 4-5 ML layers of iron deposited on Pt(111) surface at room temperature and oxidized in 1×10^{-6} Torr O₂ at 850 K. This was repeated 5-6 times and a final annealing at 1000 K assured the formation of an ordered Fe₃O₄(111) surface [23,24]. During metal deposition the sample was positively biased in order to prevent sputtering by small amount of ionized metal atoms. The deposition rate was controlled by monitoring the ion flux. Fe₃O₄ films can be converted to Fe₂O₃ by high temperature oxidation at elevated oxygen pressures (a few Torr) [24]. We have found another way of transforming Fe₃O₄ films to Fe₂O₃. The Pt(111) single crystal covered with Fe₃O₄ films were first cooled down to 100 K using liquid nitrogen cooling. Then, several tens of multilayers of water were condensed by dosing water vapor into the vacuum chamber. A small positive sample bias (100-150 V) accelerates the electrons emitted from the hot heating filament towards the backside of the crystal, as in conventional e-beam heating process; however the surface region might pick up a small portion of the sprayed electrons. Adsorbed amorphous solid water molecules then get dissociated into various fragments after being hit by these electrons. Among those fragments we believe atomic oxygen is responsible for the phase transition. Nevertheless, several cycles of water adsorption – electron spraying and incidental sample heating to 180 K and final annealing to 850 K in 1×10^{-6} Torr O₂ produced high quality ($\sqrt{3} \times \sqrt{3}$)R30° Fe₂O₃ (0001) film determined by LEED [24,25]. The phase transition was further confirmed by Fe 2p XPS and Fe L-edge/O K-edge XAS spectra generating typical Fe₂O₃ signatures (see Results and discussion section).

Bulk and surface electronic structures of the iron oxide films were investigated by XPS and XAS. In both measurements the grazing incidence angle of the incoming synchrotron light was 4°. The electron binding energies reported here are referenced to the Fermi level of Pt(111). Unless indicated in figure captions all XPS spectra were normalized to the background. Bulk and surface sensitive XPS spectra were recorded in two different measurement geometries, rotating the sample around its polar axis with respect to the electron spectrometer: As shown in Fig. 1, in the normal geometry the sample normal points to the spectrometer whereas in grazing geometry the take-off angle to the sample normal is 82°. Surface sensitive XPS measurements were performed in grazing electron emission geometry and by low kinetic energy tuning (~100 eV). For all XPS measurements polarization **E** vector is directed to the spectrometer.

Surface and near surface/bulk sensitive O K-edge XAS spectra were obtained by Auger electron yield (AEY) method. Spectra were recorded by placing the kinetic energy window of the spectrometer on the O KVV Auger transition line. Fe L-edge XAS measurements were performed similarly, using energy window of Fe LMM Auger transition. Bulk sensitive XAS measurements were also sequentially performed by total electron yield (TEY) method. In-plane and out of plane orbital components of the O 1s→2p and Fe 2p→3d excitations were probed by rotating the sample with respect to polarization **E** vector of the synchrotron radiation light. All

XAS spectra were normalized to the incident photon flux and background from pure Pt(111) was subtracted [26].

3. Results and discussions

The chemical environment of Fe cations with different oxidation states could be detected by XPS. In the case of FeO, the formal charge of Fe is 2+, and it is oxidized to 3+ as the structure is transformed into Fe₂O₃. Fe₃O₄ is on the other hand an intermediate phase which contains both Fe²⁺ and Fe³⁺ cations in an alternating manner. Fe 2p_{3/2} XPS spectra shown in Fig. 2(a) summarize above-mentioned cases. Two cations in the lattice can be distinguished in pure Fe₃O₄ spectrum as a small shoulder at 708.3 eV (Fe²⁺) and a broad peak at 710.6 eV (Fe³⁺) which perfectly aligns with the Fe₂O₃ spectrum. We note here that there is a satellite feature on the high binding energy side (now shown) due to charge transfer process from oxygen ligand in the final state. This satellite peak is rather featureless thus we focus our discussion on the main Fe 2p_{3/2} line.

Since the termination is a crucial factor in the surface activity it is important to have means to identify the surface atoms from their electronic and geometric structures. Topmost surface atoms of Fe₃O₄ could be probed by XPS, by varying photon energy (thus kinetic energy) and/or in grazing electron emission geometry. Since the inelastic mean free path of the photoelectrons goes through a minimum at about 50 eV kinetic energy and then increases with increasing energies [14], probing bulk regions and surface regions is quite possible. Fig. 2(b) shows two spectra obtained from Fe₃O₄ at two different photon energies. As the photon energy is set to 1020 eV, a reasonable number average of the surface and bulk Fe cations is obtained; the resulting spectrum is rather similar to the ones in the previous studies [20,27]. The clearly pronounced shoulder on the low binding energy side attributed to the Fe²⁺ attenuates as the photon energy is changed from 1020 eV to 810 eV and as the measurement is performed at the surface-sensitive grazing electron emission geometry. This indicates that the oxidation state of the topmost Fe layer is 3+ enriched. Further spectral deconvolution presented in Fig. 2(c) provides a more quantitative picture; Fe²⁺ component contributes 25% of the total intensity whereas this fraction goes down to 5% as the measurement geometry is more surface sensitive. It is important to note here again that the analyzed region of Fe 2p_{3/2} XPS spectrum does not represent the number of Fe atoms overall, it only illustrates lower fraction of Fe²⁺ cations in the topmost surface region.

Nominally, the Fe²⁺/Fe³⁺ ratio in the bulk Fe₃O₄ is 1/2. The measurements performed by using conventional laboratory scale X-ray sources (Al K- α radiation, 1486.7 eV) probe deeper layers thus Fe²⁺/Fe³⁺ ratios close to the bulk stoichiometry could be obtained [27]. 1020 eV however is not high enough photon energy to get bulk composition, spectral analysis already indicates surface Fe³⁺ enrichment yielding Fe²⁺/Fe³⁺ ratio equal to 1/3. Further enhancement in surface sensitivity gives rise to a surface composition which is dominated by Fe³⁺ (Fe²⁺/Fe³⁺ $\approx$ 1/20).

Even though XPS is a powerful method to determine the surface composition and oxidation states, it does not provide direct information about the local geometric coordination of the ions in the lattice. Besides, it does not give precise bulk composition since the photon energies used in this work are lower than the photon energies of the conventional sources. In this case we refer to XAS which directly probes the bonding geometry between Fe and O atoms through the unoccupied states. In various iron oxide structures Fe-O bond lengths and bond angles vary slightly [1] thus deviations are observed in valence and conduction band density of states indirectly probed by XAS. In addition, spectra representing bulk structures could be obtained due to bulk sensitivity.

The double peak O K-edge XAS structure shown in Fig. 3 is attributed to excitations to the empty Fe-O π and σ bonds that are projected onto the O 2p states [15]. Due to local symmetry relations the orbital notation of Fe-O π and σ states differs in α -Fe₂O₃ and Fe₃O₄: in an octahedral local coordination as in α -Fe₂O₃, t_{2g} and e_g orbitals represent π and σ bonding configurations, respectively. For Fe₂O₃ shown in Fig. 3(a), these are the peaks at 530.4 and 532 eV. The features at higher energies (centered at ~542 eV) are related to transitions into O 2p states hybridized with Fe 4s4p states. The relative double peak intensities depend on the polarization vector and the difference could be attributed to the out-of-plane **E** vector which is not perfectly perpendicular to the sample plane. Similar spectral interpretations based on local symmetry of the ions could in principle be done for Fe₃O₄, however complication arises because the splitting between the double peaks is not as well-resolved. For tetrahedral coordination π and σ bonds are formed between the orbitals with reversed symmetry thus t_{2g} and e_g states are split in opposite dimensions. Fe³⁺ cations in Fe_{tet} sites and Fe³⁺/Fe²⁺ cations occupying Fe_{oct} sites will all split in the presence of the oxygen ligand field and this is probably the reason for less-resolved double peak features [28]. Additional broadening could also be attributed to the multiplet effects. Fe-O local bond structure determines the energy splitting and intensities of the double peak edge structure. Ligand field exposed by oxygen and additional exchange energy determine the splitting energy of the double peaks [20]. For Fe₂O₃ the energy difference is slightly larger (1.45 eV). Distorted Fe-O bond coordination in octahedral and tetrahedral arrangements is the determining ligand field splitting factor for Fe₃O₄.

It is also important to take surface termination of Fe₂O₃ into account in spectral analysis. Along (0001) axis, the stacking sequence is Fe_{oct}-O₃-Fe_{oct} and various surface terminations have been the subject of extensive theoretical and experimental work. In UHV conditions, Fe terminated surfaces (Fe_{oct}-O₃-Fe_{oct}) have been found the most favorable [29–32]. In addition, reduced surface layers with structures resembling to Fe_(1-x)O(111) has been reported [33]. Depending on both various temperature and oxygen partial pressure conditions, oxygen (O₃-Fe_{oct}-Fe_{oct}) and ferryl (O=Fe) terminated surfaces have also been identified [24,25,34]. Since those terminations have been observed after high temperature treatments in much higher oxygen partial pressures, they will not be considered in the interpretations of spectral features related to the Fe₃O₄ surface.

Figure 3(b) compares O K-edge XAS spectra obtained from $\text{Fe}_3\text{O}_4(111)$ by AEY method in normal and grazing geometry. The spectrum obtained in normal geometry is exactly the same as the one measured with TEY method, as expected, due to the bulk sensitivities of the measurement methods. However, in the grazing geometry (near surface region is probed using out-of-plane polarized light), the peak at 532 eV slightly attenuates and the broad peak at 548 eV almost vanishes. Even though a clearly resolved peak at 532 eV does not fully appear, comparing out-of-plane polarized surface sensitive XAS spectra taken from Fe_2O_3 and Fe_3O_4 thin films suggests that local oxygen coordination in Fe_3O_4 surface atoms can be different than the bulk coordination. This is supported by the unusually small energy difference between the peaks that are attributed to t_{2g} and e_g orbitals. The relative intensities of those peaks will be explained by unique local oxygen coordination in Fe_3O_4 surface that is similar to the coordination in bulk Fe_2O_3 . The fact that surface sensitive XAS spectra are different is likely associated with the crystal field that is different for surface oxygen atoms due to terminating natures. Not only this effect determines the energy difference between t_{2g} and e_g peaks but also plays an important role in relative peak intensities. It has been suggested that the topmost Fe_{oct} and Fe_{tet} sites could be terminated by oxygen atoms [8] and the spectral change in grazing geometry could be attributed to this structural arrangement.

Fe L-edge XAS spectra of Fe_2O_3 and Fe_3O_4 shown in Fig. 4 are composed of L_3 and L_2 spin-orbit split components that are strongly influenced by the d-orbital crystal field, multiplet effects due to the Fe 3d-O 2p hybridization in the presence of the Fe 2p core-hole potentials and charge transfer effects [19]. Fe^{2+} and Fe^{3+} cations have mixed ground state potentials ($3d^6$, $3d^7L$ for Fe^{2+} and $3d^5$, $3d^6L$ for Fe^{3+} . L is an oxygen ligand hole). The multiplet interactions between the core potentials and those valence configurations at the excited state are the main reasons for the features in Fe L-edge XAS spectra. The contribution of the charge transfer from the oxygen ligand cannot be disregarded; mixed final states gives additional broadening into XAS spectra [19]. Similar to O K-edge spectra, additional complication arises for Fe_3O_4 because of two different cations located in non-equivalent sites.

Spectral features on the other hand are slightly different if bulk sensitive Fe L-edge XAS spectra of $\text{Fe}_2\text{O}_3(0001)$ and $\text{Fe}_3\text{O}_4(111)$ thin films are compared. We base our discussion on the L_3 spectral features since L_2 edge is featureless caused (mostly) by shortening of core hole life time due to Coster-Kronig Auger decay [16]. As seen in Fig. 4(a) bulk Fe_2O_3 has a rather sharp edge feature at 708.3 eV followed by a main peak at 709.8 eV and a shoulder at 713.1 eV. Fe_3O_4 spectra lack distinct features; two broad but pronounced features at 708.3 and 706.6 eV on the low energy side of the main peak seem to be characteristic for Fe_3O_4 and both films show small polarization dependence.

X-ray magnetic circular dichroism (XMCD) studies mostly focusing on the spin configuration of Fe_3O_4 reveal the individual contribution of Fe cations located in different sites to the overall Fe L-edge XAS peak shapes [18]. Octahedrally coordinated Fe^{2+} is the major contributor to the intensity of the peak at 708.3 eV and to the small shoulder at about 707 eV. All

Fe cations take part in the intensity of the main peak at 709.8 eV, but the sharp peak 708.3 eV in Fe₂O₃ sample is attributed to octahedrally coordinated Fe³⁺ cations.

As the topmost surface layers are probed several variations in spectral features are observed. Fig. 4(b) compares bulk and surface sensitive Fe L-edge XAS spectra obtained from Fe₃O₄ thin films. The pronounced peak at the low energy side of the main peak attenuates; even though not resolvable, the intensity ratios with respect to the main peaks become similar to the relative appearance of Fe₂O₃ spectra. Although surface sensitive measurements were performed in grazing electron emission geometry, the kinetic energies of Auger electrons were rather high (~565 eV). It is likely that the layer beneath the topmost surface also contributes to the XAS spectra; grazing detection geometry enhances the surface contribution which leads to this spectral change.

Our findings indicate that the core level spectroscopy distinguishes the atoms terminating the oxide surfaces. The electronic and geometric structure sensitivity gives rise to identification of the oxidation states and the bond coordination which could be compared to the known structures.

4. Conclusions

We have studied the surface terminations of Fe₃O₄(111) grown on Pt(111) by means of surface sensitive XPS, O K-edge and Fe L₃-edge XAS. Fe 2p_{3/2} XPS spectra show that the topmost surface of Fe₃O₄(111) contain much less Fe²⁺ ions in comparison to the bulk. The variations in O K-edge and Fe L₃-edge XAS spectra probing the bulk and surface regions are attributed to different local bonding coordination in the surface region. These findings indicate that the Fe₃O₄(111) surface is Fe³⁺ rich and involve octahedrally coordinated Fe cations similar to the coordination in Fe₂O₃.

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6. References

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Figure 1. XPS and XAS measurement geometry. Polarization **E** vector could be flipped and be parallel or perpendicular to the sample plane. The sample rotation around its polar axis determines the photoelectron emission trajectory with respect to the electron spectrometer. Surface sensitive XPS and XAS measurements were performed by recording photoelectrons emitted only from the topmost surface region. This was achieved by setting the take-off angle to 82° (8° from the sample plane).

Figure 2. (a) Fe 2p_{3/2} XPS spectra of (1) Fe₃O₄(111) and (2) Fe₂O₃(0001). Both spectra were recorded by setting the photon energy to 880 eV. The kinetic energy of the Fe 2p_{3/2} photoelectrons at the peak maximum was 170 eV. (b) Fe 2p_{3/2} XPS spectra of Fe₃O₄ recorded by setting the photon energy to 1020 eV (dashed) and to 810 eV (solid, which was also recorded at the grazing measurement geometry). (c) Deconvolution of Shirley background subtracted Fe 2p_{3/2} XPS spectra presented in (b). Fe 2p_{3/2} XPS spectra recorded by setting the photon energies to 1020 eV (1) and 810 eV (2) have Fe²⁺ (dashed) and Fe³⁺ (dotted) sub-components.

Figure 3. O K-edge XAS spectra of Fe₃O₄(111).and Fe₂O₃(0001) recorded by (a) TEY and (b) AEY methods. (a) In-plane and out-of-plane polarized O K-edge XAS spectra of Fe₃O₄(111) (1-2) are stacked together with XAS spectra of Fe₂O₃(0001) (3-4), respectively. (b) in-plane and out-of-plane polarized O K-edge XAS spectra of Fe₃O₄(111) recorded in normal (solid) and grazing (dashed) geometry, respectively.

Figure 4. Fe L-edge XAS spectra of $\text{Fe}_3\text{O}_4(111)$ and $\text{Fe}_2\text{O}_3(0001)$ recorded by (a) TEY and (b) AEY methods. (a) In-plane and out-of-plane polarized Fe L-edge XAS spectra of $\text{Fe}_3\text{O}_4(111)$ (1-2) are stacked together with XAS spectra of $\text{Fe}_2\text{O}_3(0001)$ (3-4), respectively. (b) in-plane and out-of-plane polarized Fe L-edge XAS spectra of $\text{Fe}_3\text{O}_4(111)$ recorded in normal (1-2) and grazing (3-4) geometry, respectively.