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Redox behavior of iron at the surface of an Fe$_{0.01}$Mg$_{0.99}$O(100) single crystal studied by ambient-pressure photoelectron spectroscopy

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ABSTRACT
We have studied the oxidation and reduction of iron in an Fe-doped MgO single crystal by O$_2$, H$_2$ and CO$_2$ using ambient-pressure XPS and NEXAFS. Surface charging of the crystal was rendered manageable by the elevated temperatures and the gas atmospheres. The oxidation state of iron was found to shift reversibly between the Fe$^{2+}$ and Fe$^{3+}$ states, with a strong asymmetry in the rates; while oxidation by O$_2$ or CO$_2$ was nearly complete at 100$^\circ$C, reduction by H$_2$ began at $\sim$300$^\circ$C, and was still incomplete at 600$^\circ$C. Grazing-incidence XRD characterization of the crystal indicated the presence of octahedral, nanoscale inclusions assigned to the magnesioferrite spinel (MgFe$_2$O$_4$). It is proposed that the redox behavior observed involves interconversion between the rock-salt (Fe$_{1-x}$Mg$_x$O) and spinel phases, with the more open lattice containing Fe$^{3+}$ enabling more rapid ion diffusion and thus more facile oxidation compared to reduction.

1. Introduction
Ternary oxides based on 3d metals and magnesium have proven useful in catalysis. For example, catalysts derived from NiO/MgO and CoO/MgO solid solutions have shown high activity and stability in steam- and dry reforming of methane, behavior linked mainly to the high resistance to sintering and to coking exhibited by the small metallic particles formed upon reduction of the materials [1–5]. Similarly high stability has been observed for Fe/MgO catalysts, which have been used in studies of ammonia synthesis [6] and Fischer-Tropsch synthesis [7], as well as studies of nanoparticle magnetism [8,9] and carbon nanotube production [10]. Mg-based oxides can also serve as support matrices for Fe$^{2+}$/Fe$^{3+}$ ions, showing activity for e.g. the high-temperature water-gas shift reaction [11], alkene dehydrogenation [12], methane combustion [13] and oxidative coupling [14].

In fundamental studies, in order to establish clear relationships between the structures of such materials and their physicochemical properties, it is desirable to employ simplified model materials and characterize these using surface sensitive analytical methods. A successful approach to studying the properties of both pure and doped MgO has been the epitaxial growth of such films on metal surfaces (most often Ag(100) or Mo(100)). Such thin films are amenable to characterization by e.g. low-energy electron diffraction and scanning tunneling microscopy [15], and studies utilizing them have yielded important insights into the surface properties of MgO and how these are influenced by dopants [16–20].

For in situ catalysis studies, however, such thin films present certain disadvantages. The melting point of silver is relatively low, and molybdenum, in addition to being difficult to prepare in a clean state, may contaminate the films, either by interdiffusion [21] or formation of volatile MoO$_3$ if oxygen is present. Here, we describe a study intended to explore the feasibility of an alternative approach: the use of a doped MgO(100) single crystal to study the surface chemistry of iron...
in MgO with in situ ambient pressure photoelectron spectroscopy (AP-PES). As a first step, our goal was to determine whether such measurements could produce useful data and to investigate the changes in dopant chemical state induced by the gas environment. The single crystal used was doped with Fe at a level of 1% of the total metal content, giving the ideal ferropericlase bulk structure a formula of Fe$_{0.01}$Mg$_{0.99}$O.

We conducted Fe$_2$XPS and NEXAFS measurements, which yield information about the oxidation state at different depths, exposing the surface to O$_2$, CO$_2$ and H$_2$ at a range of temperatures. Grazing-incidence X-ray diffraction, though not providing surface specific information in this case, furthermore sheds light on the state of iron in the bulk of the crystal.

2. Methods

Ambient-pressure photoelectron spectroscopy measurements were performed at beamline 9.3.2 at the Advanced Light Source, Lawrence Berkeley National Laboratory [22]. The endstation at this beamline consists of a two-chamber vacuum system including a preparation chamber equipped with an ion gun for Ar$^+$ sputtering, and an analysis chamber where the differentially-pumped Scienta R4000 analyzer is mounted. High pressure measurements were made by manually backfilling this chamber with the respective gases to a total pressure of 0.1 torr through leak valves. XPS measurements were performed with a fixed incident photon energy of 800 eV and 100 eV pass
energy. Binding energies are referenced to the O1s peak, assumed to be fixed at 530.5 eV [23]. Estimation of the surface Fe concentration of the sample was performed by comparing the integrated Fe2p and O1s peak intensities from a single survey scan acquired with a beam energy of 800 eV. The raw Fe2p/O1s ratio was corrected for the difference in photoionization cross sections at 800 eV ($\sigma_{Fe}/\sigma_{O} \approx 5.4$ [24]) and in the electron mean free paths at the different kinetic energies ($\lambda_{Fe}/\lambda_{O} \approx 0.8$ [25]).

NEXAFS spectra of the Fe-L$_{2,3}$ edge were acquired by measuring the secondary electron background with a pass energy of 200 eV, giving a $\sim 15$ eV window at kinetic energies below those of the Fe-LMM Auger emission, at 550–590 eV, adjusted at each condition to compensate for sample charging, which was checked by measuring the position of the Mg2p peak at the start of the scan. The offset was between 0 and 25 eV, depending on temperature. The photon energy was calibrated by measurement of the difference in kinetic energy of photoelectrons excited by the 1st and 2nd harmonic components of the beam at the starting point of the energy scan. For the measurements performed on the lightly-sputtered crystal, the Au4f$_{7/2}$ peak from a gold foil was used for this purpose, while for the experiments on the thoroughly-cleaned crystal (performed during a later beamtime session), the O1s peak of the sample itself was used. This difference apparently resulted in an offset of $\sim 0.5$ eV between the two sets of measurements, which we suspect is due to a small miscalibration of the analyzer. For consistency the energy scale in NEXAFS measurements of the lightly sputtered crystal has been shifted by +0.5 eV. Note, however, an uncertainty in the absolute energy scale of approximately this magnitude.

The Fe$_{0.01}$Mg$_{0.99}$O(100) single crystal, grown in an arc furnace with iron added to the MgO melt, was provided by SurfaceNet GmbH. The 10 mm $\times$ 5 mm $\times$ 2 mm rectangular crystal was oriented and polished on one side in the (100) orientation. For ambient-pressure photoelectron spectroscopy measurements, the crystal was mounted to a transferable sample platform with integrated heater. A K-type thermocouple was pressed against the MgO itself is expected to be inert, so our initial presumption was that shifts in these peaks would be attributable entirely to electrostatic charging, so that their positions could be used as energy references for the iron XPS spectra. Comparing the spectra obtained at the lowest temperature (Figure 1(a)), with that at the highest (Figure 1(b)), we note a shift of $\sim 19$ eV accompanied by slight broadening of the peaks ($\sim 0.4$ eV). The O1s and Mg2p peaks shift together with temperature, and their difference in binding energy is nearly constant (Figure 1(c)), growing by ca. 0.2 eV with increasing temperature (Figure 1(d)), consistent with electrostatic retardation. Thus it appears that the surface charging, though substantial at the lowest temperatures, is sufficiently uniform that it can be tracked based on the MgO peaks and the binding energies of Fe2p XPS spectra corrected accordingly.

### 3. Results

#### 3.1. Beam-induced charging effects

Magnesium oxide is an insulator with a large band gap, and shows significant charging effects when exposed to the X-ray beam. The emission of photoelectrons causes buildup of positive charge at the surface, lowering the emitted electrons’ kinetic energies and thus increasing their apparent binding energies. The first XPS measurements made on the Fe$_{0.01}$Mg$_{0.99}$O crystal in vacuum and at room temperature showed shifts of up to $\sim 130$ eV, with substantial peak splitting indicative of inhomogeneous charging. Introduction of H$_2$ gas followed by stepwise heating led to a gradual decrease in the charge buildup, and at $\sim 500$ °C, the peak splitting was removed and good-quality XPS spectra could be obtained. Presumably this treatment caused removal of residual defects from the sputtering process or exposure to air, or to redistribution of species such as cations and vacancies associated with Fe, increasing the sample’s conductivity and allowing more uniform charge distribution. In subsequent measurements, obtained in gas atmospheres of 0.1–0.2 torr and at temperatures between 100 °C and 600 °C, the binding energy offsets of O and Mg peaks were found to depend on the sample temperature, but were limited to $< 25$ eV.

Figure 1 shows O1s and Mg2p spectra obtained in H$_2$ at different temperatures. Under these conditions, the MgO itself is expected to be inert, so our initial presumption was that shifts in these peaks would be attributable entirely to electrostatic charging, so that their positions could be used as energy references for the iron XPS spectra. Comparing the spectra obtained at the lowest temperature (Figure 1(a)), with that at the highest (Figure 1(b)), we note a shift of $\sim 19$ eV accompanied by slight broadening of the peaks ($\sim 0.4$ eV). The O1s and Mg2p peaks shift together with temperature, and their difference in binding energy is nearly constant (Figure 1(c)), growing by ca. 0.2 eV with increasing temperature (Figure 1(d)), consistent with electrostatic retardation. Thus it appears that the surface charging, though substantial at the lowest temperatures, is sufficiently uniform that it can be tracked based on the MgO peaks and the binding energies of Fe2p XPS spectra corrected accordingly.

#### 3.2. Lightly sputtered crystal

Initial measurements were made following minimal preparation of the crystal. After introduction to the UHV system it was sputtered gently (1 $\times$ 10$^{-6}$ Ar, 500 V, 5 mA for 5 min), then heated in O$_2$ (1 $\times$ 10$^{-5}$, 500 °C,
30 min) before introduction to the ambient-pressure measurement chamber. After heating treatments first in H₂, then in O₂, which resulted in removal of residual carbon, the crystal exhibited trace contamination by calcium and phosphorus, as well as a surprisingly large proportion of Fe; comparison of relative areas of the O1s and Fe2p₃/2 peaks, after correction for the difference in photoionization cross section [24] yielded an iron concentration of 3–5 % (varying with changes in gas atmosphere and temperature). We attribute the large concentration of Fe (significantly higher than after extensive sputtering, as discussed below) to segregation of iron to the surface promoted by oxygen in the air [27]. The variations in Fe signal intensity are suggestive of either segregation/desegregation of Fe or to changes in the morphology of Fe-containing surface features. As similar fluctuations were not observed for the more heavily-sputtered surface, however, this behavior appears unique to the iron-enriched surface present initially and was not investigated further.

Nevertheless, initial test measurements were carried out on the sample in this state. Representative XPS and NEXAFS spectra corresponding to the most oxidized and most reduced states observed are plotted in Figure 2(a) and (b), respectively. The XPS spectra show a shift of 1.4 eV between the oxidized and reduced states as well as distinct satellite features which are characteristic of compounds containing pure Fe²⁺ or Fe³⁺ (mixed valence compounds such as Fe₃O₄ tend to show a featureless background due to overlap of the satellite peaks) [28]. The absolute binding energies, at ∼710.4 eV and ∼711.8 eV, are higher (ca. 1 eV) than expected for these states. Though the reason for this is unclear, the observed changes in binding energy are consistent and based on the satellite structure and NEXAFS spectra we are confident that the relative shifts give reliable indications of changes in oxidation state.

Corresponding Fe-L₂,₃ NEXAFS spectra are plotted in Figure 2(b). These spectra show a difference in energy of the L₃ peak maxima between the oxidized and reduced states of ∼1.7 eV, corresponding reasonably well to the difference observed between Fe³⁺ and Fe²⁺ as reported previously [29,30]. A slight shoulder at the low energy side of the L₃ peak measured in O₂ is intrinsic to Fe³⁺, and likewise a small feature on the high energy side of the peak measured in H₂ is intrinsic to Fe²⁺. The absence of more distinct features in the respective spectra indicate essentially pure Fe²⁺ and Fe³⁺ phases.
We note here that the difference in the nature of the photoelectrons collected for the XPS and NEXAFS spectra causes these measurements to reflect the composition of the surface at different probe depths; while in XPS (collected here with a photon energy of 800 eV), the ~90 eV photoelectrons exhibit inelastic mean free paths of ~0.6 nm [25], so that assuming a uniform distribution of Fe, the majority of the signal originates in the outermost layer of about this thickness. The NEXAFS measurements, on the other hand, utilize electrons derived from Fe Auger emission, but which have lost a small amount of energy due to inelastic scattering. This loss of energy causes the escape depth to increase, so that the information depth is intermediate between that of elastic Auger electrons and that of the secondary electrons which make up the bulk of the signal in a total electron yield measurement, or roughly in the range of 1–3 nm (see, for example, Ref. [31]). The measurements here indicate that the iron oxidation state is uniform over the outermost few nm of the crystal. As will be shown below, this is not the case for the more extensively sputtered crystal.

### 3.3. Heavily sputtered crystal

To produce a surface that was free from impurities and exposed iron at a concentration more reflective of the bulk composition, the crystal was exposed to a larger fluence of Ar$^+$ ions at a higher beam energy (5 × 10$^{-6}$ Ar, 1500 V, 10 mA for 30 min), annealing the crystal at 600°C for 10 min after each 10 min of sputtering. An overview spectrum of the crystal following this procedure is shown in Figure 3. The Ca and P contaminations observed initially were not present; the only contaminant observed was Ar which was embedded in the cleaning process. The Fe concentration was also reduced; measurement of the peak area ratio yields a concentration of 1 %, matching the expected bulk composition well.

To systematically study the oxidation state of iron in this crystal, a series of measurements were conducted where the crystal was heated stepwise in 0.1 torr H$_2$, O$_2$, or CO$_2$, following a treatment in O$_2$ or H$_2$ at ~600°C, intended to oxidize or reduce the iron to the greatest extent possible. At each temperature, the Fe2p XPS and Fe-L$_{2,3}$ NEXAFS spectra were acquired. The results are plotted in Figure 4. Due to the small Fe concentration, large integration times were necessary to produce spectra with adequate signal-to-noise ratios in the XPS spectra. Each spectrum shown is an average of 5 sweeps, each of which was corrected for shifts in energy (due to drift in the temperature) by a measurement of the O1s peak. The total measurement time for a single condition was approximately 90 min.

The measurements obtained while heating the oxidized surface in H$_2$ are plotted in Figure 4(a), and (b). Here we can see that initially at 100°C, the iron is predominantly in an oxidized state. At the surface, XPS shows a spectrum corresponding to essentially pure Fe$^{3+}$. In the NEXAFS spectrum, a small shoulder component suggests a small amount of Fe$^{2+}$ deeper in the crystal. Beginning above ~200°C, the XPS peaks begin to shift to lower binding energy, and by 473°C they reach the position corresponding to Fe$^{2+}$. The corresponding NEXAFS spectra exhibit similar behavior, though changes occur at higher temperatures; the first hint of reduction of Fe here is observed between 458 and 524°C, where the intensity of the low-energy component begins to increase. At 592°C, the highest temperature attainable under these conditions, the Fe$^{2+}$ and Fe$^{3+}$ components are roughly equal in intensity. With time, the extent of reduction of the crystal increases, but even after 1 hour in H$_2$, the Fe$^{3+}$ component is still present.
The spectra obtained during oxidation of the crystal by O$_2$ (Figure 4(c), and (d)) and CO$_2$ (Figure 4(e), and (f)) are similar to each other but drastically different from those obtained during reduction. In both cases, already at 100°C both XPS and NEXAFS show predominantly Fe$^{3+}$, and the XPS shows little change with temperature. The NEXAFS spectra show a subtle decrease in the Fe$^{2+}$ component as subsurface Fe is oxidized. In the case of CO$_2$ exposure, control spectra acquired during the experiment at 310°C and 520°C showed no signs of carbon accumulation.

### 3.4. Grazing-incidence X-ray diffraction

In an attempt to gain some structural information about the surface of the crystal during these oxidation and reduction treatments, we also conducted in situ X-ray diffraction measurements at the high-energy diffraction beamline P07 at PETRA-III. Here the crystal could be sputtered and annealed, exposed to high-pressure gas environments and heated, similarly to the AP-PES experiments. We were unable to detect surface-specific diffraction components, which appear as distinct rods in the out-of-plane direction of the HESXRD patterns.

**Figure 4.** AP-XPS (a,c,e) and NEXAFS (b,d,f) spectra acquired in different gas environments for a series of increasing temperatures. (a,b) Heating in H$_2$ following oxidation in O$_2$ at 600°C. (c,d) Heating in O$_2$ following reduction in H$_2$ and 600°C. (e,f) Heating in CO$_2$ following reduction in H$_2$ and 600°C.
Figure 5. X-ray diffraction pattern of the Fe-doped MgO(100) crystal, obtained in grazing incidence with 78.9 keV photons. The image shown was generated by taking the maximum value for each pixel measured from an azimuthal scan of the crystal. Diffraction angles for MgO are indicated in blue and those for MgFe$_2$O$_4$ are shown in red. Miller indices are specific to the respective compound. Inset: enlargement of one of the spinel [113] reflections. Note the fringes extending in [111] directions, indicative of an octahedral crystal shape with dimensions on the order of 10 nm.

[32]. Most likely the surface prepared in this way was too rough to produce coherent surface diffraction. The measured diffraction pattern nevertheless showed components distinct from that of the pure MgO crystal. The measurement obtained by integration of an azimuthal scan is displayed in Figure 5. The (002) reflection normal to the surface was blocked by a piece of tungsten in order to protect the detector from the high scattered intensity at this position. Equivalent [200] reflections in the plane also produce some visible signal.

The remaining spots can be attributed to a spinel lattice with a unit cell double the size of the MgO. The cubic spinel lattice is aligned with that of the MgO. The most likely compound giving rise to these features is magnesioferrite (MgFe$_2$O$_4$), which is the stable phase for a magnesium-iron-oxide in air and whose fcc oxygen sublattice is nearly identical to that of MgO. Close inspection of the diffraacted spot profiles (Figure 5 inset) shows broadened spots with visible interference fringes, indicating the spinel phase takes the form of monodisperse nanoparticles with diameters on the order of 10 nm. The fringes are seen most prominently extending along [111] directions, indicating that these nanoparticles are octahedral in shape, bounded by [111] planes. Exposure of the crystal to H$_2$ and O$_2$, respectively, at temperatures up to $\sim$600 $^\circ$C had no noticeable affect on the intensity of these features, nor did it lead to any new diffraction features. It is therefore concluded that the spinel crystallites observed are inclusions incorporated within the MgO.

4. Discussion

The observation of inclusions in the crystal with a spinel structure is reasonable, thermodynamically, considering the phase diagram of the Fe-Mg-O system [33]. Under the conditions of crystal growth, from the molten state in the presence of air, the stable phase is the rock-salt ferropericlase, i.e. a solid solution between FeO and MgO. Upon cooling in air, however, the majority of the iron should precipitate as MgFe$_2$O$_4$. Experiments reported by Schaefer and Brindley showed that oxidation of Fe$_x$Mg$_{1-x}$O single crystals at high temperatures led to substantial formation of MgFe$_2$O$_4$ inclusions, concentrated especially at the surface [27]. Although prior to the experiments reported here the crystal was not intentionally heated in oxygen, the time and/or the cutting and polishing process may have allowed for the concentration of Fe at the surface, as observed in our XPS measurements.

We interpret the ambient pressure XPS and NEXAFS measurements in terms of a similar transformation: between the rock salt Fe$_{2-x}$Mg$_x$O under reducing conditions and spinel MgFe$_{2+}$O$_4$ which is the stable state under oxidizing conditions. The presence of Fe$^{3+}$ as isolated species is possible as well, if kinetic limitations prevent condensation of these species into the clusters of the spinel phase. Weeks et al. [34] studied the concentration and state of such species in doped MgO by electron paramagnetic resonance and found that ion mobility was sufficient to enable aggregation of Fe$^{3+}$ already at 350 $^\circ$C, and that for Fe concentrations as high as that studied here, such isolated species occurred in very low abundance.

The drastic difference we observe in the rates of oxidation and reduction is intriguing; considering the observation of a gradient in the Fe$^{3+}$ content during reduction, the limiting factor appears to be mass transfer within the solid, rather than the reaction at the surface. Also in the case of oxidation, the fact that similar behavior is observed for O$_2$ and CO$_2$ suggests that surface processes are rapid under these conditions. The more facile oxidation of the crystal is possibly linked to the creation of cation vacancies which accompanies the formation of Fe$^{3+}$ and enhances diffusivity in the crystal [35]. The rock-salt crystal structure exhibits
dense occupation of the octahedral lattice sites and consequently provides low mobility; the elimination of cation vacancies near the surface of the crystal may thus prevent further reduction deeper below the surface. We note here that similar hindrance to reduction was not observed for the lightly-sputtered crystal which exhibited Fe enrichment at the surface. We speculate that in this case clusters of magnesioferrite were formed atop the MgO crystal which reacted more easily than the iron which was embedded in the crystal and exposed after sputtering.

Although one of the primary motivations for this work was the study of metallic particles formed by complete reduction of the iron, metallic iron was not observed under any of the reaction conditions. Apparently the hydrogen pressure and/or sample temperature were too low for this reduction to take place to a detectable extent. It may also be that the low concentration of Fe in the crystal also hinders complete reduction to the metallic state. In studies of powder samples it was observed that larger proportions of Fe were reduced at higher total Fe loadings, which would be consistent [8,36]. Further research in this direction may either make use of Fe nanoparticles produced by physical vapor deposition or of more iron-rich oxide phases which could be produced by e.g. growth of Fe3O4 atop MgO(100) and subsequent calcination to promote intermixing.

The formation of magnesioferrite nanocrystals as inclusions in the bulk of MgO is also intriguing and suggests an interesting avenue for further study. Though perhaps of limited relevance for catalysis, such nanoparticles should be expected to exhibit ferromagnetism or superparamagnetism. It is conceivable that by varying the Fe concentration and/or treatment procedures the sizes of these clusters can be varied, enabling systematic study of their properties.

5. Conclusions

We have demonstrated the feasibility of applying in situ ambient-pressure photoelectron spectroscopy to the study of doped MgO single crystals. Although charging is significant, useful chemical information can nevertheless be obtained about the dopant. Under oxidizing and reducing conditions, we have shown that the oxidation state of Fe can be followed, and it was observed to transform between Fe2+ in H2 and Fe3+ in O2 or CO2. The process of reduction is significantly slower than that of oxidation, which is speculated to reflect the low abundance of metal ion vacancies in the reduced phase. X-ray diffraction measurements show that Fe3+ precipitates in the bulk of the crystal to form nanocrystalline inclusions with well-defined shapes and a narrow size distribution. The redox process occurring at the surface is proposed to involve transformation between ferropericlase and magnesioferrite phases.

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Disclosure statement

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