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Core-exciton-induced desorption from MgO

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Core-exciton-induced desorption of O^+ and H^+ from MgO(100) and MgO(111) has been observed using photon excitation energies spanning the O K edge. Electron-yield data from partially oxidized Mg implies that these states are localized in the near-surface region. O^+ and H^+ desorption results from the decay of different O core-exciton states as well as the states produced by interband transitions. The O excitonic levels are interpreted in terms of their related atomic origin.

Recent investigations into the mechanisms of ion desorption induced by electronic transitions have focused on understanding the fundamental electronic excitations that decay to produce a desorbing species. In this Rapid Communication, we report the first observation of ion desorption from O core-excitation states. Exciton-induced ion desorption has been observed previously,^{1,2} but this is the first observation of desorption stimulated by an exciton formed on the *ligand* (as opposed to the metal). In addition, it is the deepest such desorption-inducing exciton observed. The decay of this state to produce a desorbing ligand is therefore fundamentally different.

We have observed core-exciton-induced desorption of O^+ and of H^+ from MgO with photon excitation energies spanning the O K edge. We present evidence for the contribution of several excitonic states to the desorption of O^+ and show that these states are different from those giving rise to H^+ desorption. Electron yield data from partially oxidized Mg imply that these excitations are localized in the near surface region.

In MgO, surface and bulk Mg^{2+} excitonic states have been observed in electron energy loss spectra (EELS) following excitation of the Mg $2s$ and $2p$ levels; the excitonic levels at the surface were found to be Stark shifted by the strong change in Madelung potential induced by the surface.³ The deeper O K core excitons in MgO, produced by photon absorption, have, however, not been studied. These core excitons are expected to be consistent with the Frenkel model and they are not expected to be mobile; the overlap of O- $1s$ core-electronic wave functions is small and prevents significant hole tunneling between O cores.

The experiments were performed at the wiggler-undulator beamline at the Hamburg Synchrotronstrahlungslabor (HASYLAB) on the Doppel-Ring Speicherring (DORIS) synchrotron storage ring using

the Flipper monochromator. The MgO(100) single crystal surface was cleaved in air and prepared in ultrahigh vacuum (UHV) by sputtering and annealing. MgO(111) was aligned ($\pm 0.5^\circ$) by Laue backscattering, cut, and polished; it was prepared similarly in UHV. MgO(111) has been shown to facet on annealing to form (100) planes.⁴ Despite the presence of significant numbers of facet edge sites (defects), results from Mg(111) were essentially identical to those from the (100) surface. Only data from Mg(100) are presented. The partially oxidized Mg was prepared by evaporating Mg onto stainless steel and exposing to a background of O_2 . Photoelectron spectroscopies from the single-crystal oxide were not reliable due to charging of the sample surface under photon impact; however, the thin oxide formed on the Mg metal was not observed to charge appreciably.

Positive-ion spectroscopies were performed with a time-of-flight (TOF) analyzer. A -1.4 kV extraction voltage mitigated the effect of the (positive) sample charging on the ion spectra. Ion yields were obtained by monitoring the peak intensity at the proper delay from the photon pulse as the incident photon energy was varied.

In addition to the ion peaks in the TOF spectrum, a "prompt" peak was observed with no measurable delay. Recent experiments show that this peak at the O K edge is mainly fluorescence superimposed on a background of scattered light.⁵ Light reflected specularly from the sample did not enter the TOF analyzer.

Figure 1 shows the desorption spectra (O^+ - and H^+ -ion yields) from sputtered and annealed MgO(100) as well as the (prompt) fluorescence yield over the O K edge. The lower part of Fig. 1 shows an electron energy loss measurement made by transmitting 60-keV electrons through 500 Å of MgO microcrystals.⁶ This is primarily a bulk energy-loss measurement. The onset in O K core

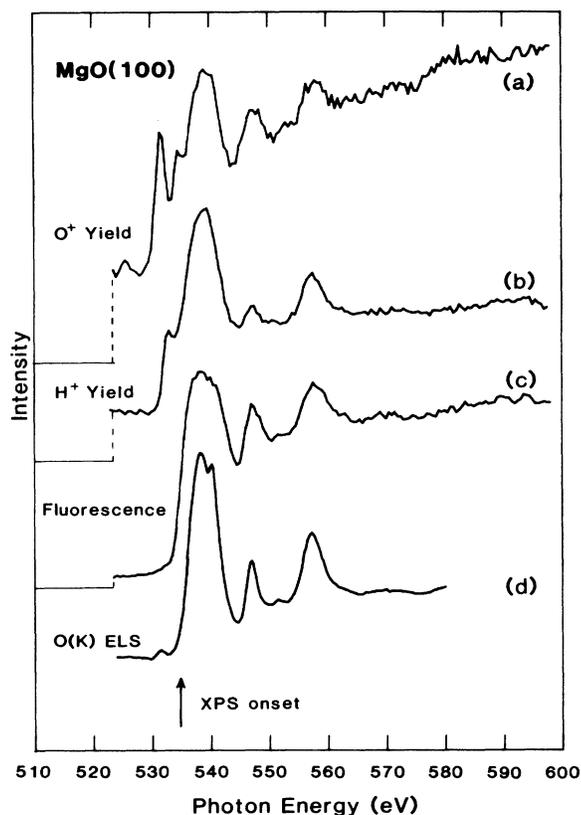


FIG. 1. Photon excitation spectra from annealed MgO(100) over the O *K* threshold: (a) the O⁺ ion yield, (b) H⁺ ion yield, (c) fluorescence (prompt) signal, (d) O(*K*) electron energy loss spectrum from Ref. 6 obtained with 60-keV primary electrons in transmission through MgO microcrystals. The zeros for spectra (a)–(c) are indicated. The arrow indicates the O 1*s* excitation onset obtained from Ref. 7.

excitation to unoccupied conduction band states in the bulk is indicated by the arrow at 534.9 eV. This value was obtained by taking the MgO (1*s*) binding energy measured by Fuggle,⁷ the location of the upper edge of the O(2*p*) band, and the measured 7.77-eV band gap between the occupied O(2*p*) levels and unoccupied conduction bands of bulk MgO.^{7,8}

Much of the same structure is apparent in all of these curves; however, there are striking differences. A dominant O⁺ peak at 531.6 eV occurs at a lower energy than the onset in the fluorescence or primary EELS structure. There is also a shoulder at 534.6 eV in the O⁺ desorption curve. The signal to noise does not permit us to identify unambiguously an additional feature at 525 eV. The peak at 531.6 eV in the O⁺ spectrum appears at the same energy as the small feature observed *before* the onset of core-to-band excitation in the EELS spectrum. Korringa-Kohn-Rostoker band-structure calculations in Ref. 6 produce results in substantial agreement with the observed EELS structures except for the feature below 533 eV, which is interpreted to be due to an excitonic state.⁶ The H⁺ yield also shows a distinct peak before the primary

core-to-conduction-band transition onset. The fluorescence spectrum lacks a distinct peak at this energy. The remaining structure between 533 and 564 eV in all of these spectra are located at the same energies.

In Fig. 2, the O⁺ and H⁺ ion yield curves from MgO(100) are again shown near the onset in O *K* excitation. The O⁺ near-edge structure, Fig. 2(c), is decomposed into a sum of Gaussians at 531.6 and at 534.6 eV. Subtraction of the Gaussians from the measured data reveals an onset in the interband transitions producing desorption at 534.9 eV, identical to the onset in x-ray photoemission spectroscopy.⁷ The H⁺ near edge structure, Fig. 2(d), is decomposed as the O⁺; however, only the single feature at 533.4 eV is clearly evident. If an additional (and unresolved) feature located at 535.0 eV were to be removed from this spectrum, as shown, the onset in interband transitions suggested by the H⁺ yield would be

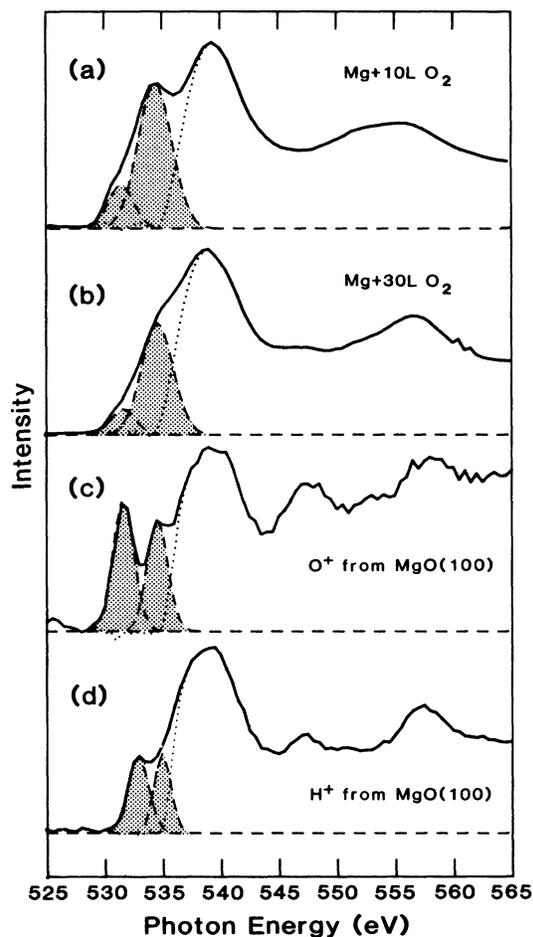


FIG. 2. Electron-yield and ion-emission intensity vs incident photon energy: (a) electron yield from evaporated Mg exposed to 10 L O₂, (b) Mg exposed to 30 L O₂, (c) O⁺ yield from MgO(100), (d) H⁺ yield from MgO(100). The data in (c) and (d) are the same shown in Fig. 1. The spectra are decomposed into the excitonic desorption contribution given by the dashed Gaussian peaks. The dotted curves are obtained by subtracting the Gaussian peaks from the data.

535.0 eV; essentially the same as that observed for O^+ .

Also shown in Fig. 2 are the electron total yield curves measured from an evaporated Mg film exposed to 10 Langmuir ($L, 1 L = 10^{-6}$ Torr sec) O_2 , Fig. 2(a), and to 30 L O_2 , Fig. 2(b). Prior to O_2 exposure, structure in the electron yield from evaporated Mg was not observed in this photon energy range. The Gaussians used in the 30 L exposure data are located at the same energies as the corresponding O^+ features, but those in the 10 L exposure data, Fig. 2(a), are located 0.1 eV to lower photon energy. If these peaks are subtracted from the data, the interband onsets would be 535.1 and 534.8 eV for Figs. 2(a) and 2(b), respectively.

The data in Figs. 2(a) and 2(b) show the progressive development of the O K photoabsorption as the surface changes from a thin surface oxide (at 10 L O_2) to a more bulklike oxide layer. At saturation oxygen exposure, a Mg film develops an oxide layer thickness of $7 \pm 3 \text{ \AA}$;⁷ this is nearly achieved with the 30-L exposure. At the lower O_2 exposure, the electron emission at the O K edge is dominated by emission from the surface and shows a strong contribution from the pre-edge features. The emission from the thicker oxide layer shows a relative increase in the contribution due to bulk interband transitions. Since the electron attenuation length at this energy is approximately 22 Å (Ref. 9) (nearly three times the oxide layer thickness), we can compare directly the relative intensities of these different transitions for the two O_2 exposures. The spectra are contrasted by comparing the ratio of the integrated Gaussians to the residual intensity (less the constant background) in the electron yield data from 530 to 550 eV. This shows that there is a 34% drop in the pre-edge (Gaussian) contribution for the 30 L O_2 exposure relative to the 10 L O_2 exposure. This implies that exciton production is more probable in the near surface region.

Using photon energies spanning the Mg $1s$ level, we were unable to detect evidence of Mg core excitons in desorption or in the electron yield from the oxidized Mg film. This indicates that the band-gap excitations that we observe are strictly oxygen excitations.

The features decomposed in Fig. 2 using the Gaussians are identified as being due to desorption and electron emission from the decay of excitonic states. We describe these states in terms of their atomic character. Since dipole-allowed transitions should be most intense, we identify the peak at 531.6 eV in the O^+ yield as due to a $1s^2 2s^2 2p^6 \rightarrow 1s^1 2s^2 2p^6 3p^1$ core-excitonic state. The peak at 534.6 eV in the O^+ yield is proposed to be due to $1s^1 \cdots np^1$ ($1s^1 2s^2 2p^6 np^1, n > 3$) excitations. The feature at 532.9 eV in the H^+ desorption yield is identified as a $1s^1 \cdots 3p^1$ O core-excitonic state of OH^- for the reasons discussed below.

In the extremely ionic environment of MgO, the O is in a very nearly 2^- state; this is almost unchanged at the surface. This implies that an initially excited surface O^{2-} must *autoionize* and lose three electrons in order to desorb as an O^+ . In such a decay, the excitonic electron is less likely to be a participant (which would result in a one-hole final state) than it is to remain as a spectator to the decay. A two-hole-one-electron intermediate state (O^-) will re-

sult from the $1s^1 2s^2 2p^6 3p^1 \rightarrow 1s^2 2s^2 2p^4 3p^1$ decay. As in the *interatomic* Auger decay mechanism for desorption from TiO_2 ,¹⁰ a finite probability exists for this *intraatomic* Auger decay to involve an additional $2p$ electron resulting in a $1s^2 2s^2 2p^3 3p^1$ state (an intermediate O^0). When the O $1s$ core hole becomes occupied in the Auger decay, the exciton electron state is no longer allowed. The escape of this electron from the intermediate O^0 will result in the formation of an O^+ ion.

When the core hole is neutralized in the Auger decay, the binding energy of the exciton electron to the core hole is lost and this energy may assist in the escape of the excitonic electron. If we estimate this binding energy as the difference between the 531.6 eV peak and the onset in the fluorescence (at 533.5 eV), the exciton binding energy would be 1.9 eV.

Should the exciton electron escape, the O^+ will clearly be in a repulsive surface Madelung potential. Calculations of the MgO(100) Madelung potential indicate that the ion will have in excess of 23-eV potential energy at an in-plane surface site;¹¹ however, lattice relaxation and electronic screening effects during ion escape are expected to reduce this energy.¹² If the O^+ were to desorb from a Mg atop site, the potential energy there is only 0.9 eV.¹¹

The question arises as to why we should see exciton-induced desorption and yet see a small fluorescence or EELS exciton signature. One reason is that the desorption process involves excitations only at the surface while the fluorescence and EELS spectra are primarily bulk sensitive. The EELS spectrum does show a small excitonic feature, though. This spectrum includes some contribution from surface regions, an amount that we estimate to be about 2%,¹³ and therefore the feature may be due entirely to surface excitons.

The enhanced intensity of the exciton peak observed in the desorption implies that this state is either produced more efficiently on the surface than in the bulk (as indicated by the electron yield data) or that the matrix elements involved in the decay of the exciton result in a higher probability for positive ion production than those involved in the decay of an interband excitation.

The H^+ -ion yield also shows excitonic structure; however, only one distinct state is clearly resolved at 532.9 eV. The presence of structure in the H^+ yield near the O K core level is not surprising since calculations show that H adsorbed on MgO(100) is stable in an OH^- species.¹⁴ In order for the OH^- to dissociate and produce H^+ it is only necessary that the decay of the O core exciton places the radical into an antibonding configuration. The subsequent trajectory along the repulsive interatomic potentials then results in desorption of H^+ . The energetic shift between the O^{2-} and OH^- excitonic levels is to be expected since the formation of the OH bond produces hybridized orbitals.

In conclusion, we have shown that O^+ and H^+ desorption from MgO(100) surfaces in the energy range spanning the O K level arise from two distinct mechanisms: the Auger decay of O core excitons and the desorption of O^+ due to the decay of an excited state formed by an interband transition. Electron yield data from partially oxidized Mg imply that excitons are produced more

efficiently at the surface. The H^+ originates from surface OH^- species. These data also show that the desorption due to excitonic states of OH^- is different from those of the O^{2-} of MgO. This demonstrates the existence of a new excitation-producing ion desorption and site selectivity that allows one to distinguish desorption from different surface species.

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