Electronic structure of MgO studied by angle-resolved ultraviolet photoelectron spectroscopy

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We report on the electronic structure of MgO using angle-resolved ultraviolet photoelectron spectroscopy. The commonly catastrophic charging effects have been managed by means of an electron flood-gun. Features in the spectra, taken from the MgO(100) surface, can be assigned to a superposition of angle-integrated bulk transitions and direct bulk transitions. The results are in accordance with ab-initio bulk band-structure calculations.

1. Introduction

MgO is an important support for various metal catalysts and thin films. Understanding of the geometric and electronic properties of the clean and adsorbate-covered surface, interface and bulk as well are required [1]. The existence of defects, dopants and interfaces might play a crucial role. MgO could also serve as an interesting comparison material for transition-metal oxides having the same rocksalt crystal structure [1]. It is known that the electronic structure of compounds like NiO, CoO and MnO are dominated by many-body effects [2–8] and that therefore the ARUPS data [6,9,10] are complicated to interpret. The electronic structure of MgO on the other hand, can be described within a one-particle framework. The valence band consists mainly of highly dispersive O 2p derived states and ARUPS data on MgO can therefore serve as an estimate for the contribution of oxygen states in the spectra of the transition-metal oxides in the limiting situation of zero hybridization of the oxygen with the transition-metal 3d states.

Surface science research is facilitated by the fact that it is relatively easy to obtain a clean and well-ordered MgO(100) surface under ultra-high vacuum conditions. The surface has proven to be very stable under various forms of irradiation. However, surface-sensitive techniques using low energy charged particles are hindered by the fact that MgO is such a good insulator with a band-gap of 7.8 eV.

Various forms of diffraction and scattering techniques have been used in order to characterize the surface geometry and its dynamical properties. They include low energy electron diffraction (LEED) [11–15], reflection high energy electron diffraction (RHEED) [16–18], high resolution electron energy loss spectroscopy (HREELS) [19–21], thermal He atom diffraction [22–24], impact-collision ion scattering spectroscopy (ICISS) [25] and neutron scattering [26,27]. Attention has been focused to overcoming charging problems for techniques involving low energy electrons (less than 100 eV). Solutions such as primary electron energy modulation in LEED [14] and co-irradiation of high energy electrons in HREELS [19,20], have been developed. Along with the experiments, a number of theoretical works on structure and dynamics has been conducted [28–35].

Electronic structure studies on MgO have been carried out using X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) and X-ray absorption near-edge structure (XANES). Much of the attention has been paid to
bulk properties and to this end, powders [36], thin films [37-39] and also single crystals [40-42] have been used. XPS and AES were also used to investigate the growth mechanism and chemical state of Cu evaporated on MgO(100) [43,44]. More detailed studies on the valence/conduction bands of both bulk and surfaces were mainly done by electron energy loss spectroscopy (EELS) with primary energies above 100 eV [43,45-51]. The data were interpreted in terms of excitonic excitations and joint density of valence and conduction states, including surface and vacancy induced effects. A more straightforward measurement of the valence band density of states using ultra-violet photoelectron spectroscopy (UPS) is hampered by severe charging problems. Only few UPS studies exist [52,53], where use was made of a flood-gun. Up to now however, no angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) data were available, which would have provided direct information about translational symmetry effects in the bulk, surface and interface electronic structure. Such a direct experimental verification for results from various theoretical calculations on bulk [54-57], surface [58-60] and (surface) impurity [61-63] electronic structure is called for.

In this paper we present an ARUPS study on the clean MgO(100) surface. In managing the charging problems, we use a flood-gun which provides a high current of electrons with energies sufficiently low in order not to distort the angle dependence of the emitted photoelectrons. Another method would be the enhancement of the charge mobility by heating the sample above approximately 500°C [64]. However, this would not be suitable for future studies on MgO surfaces in relationship with various overlayer structures. The flood-gun technique could be useful for studying various wide band-gap (\( \geq 4 \) eV) oxides and halides. NaCl is such an example, which is the only wide band-gap material known to us up to now, on which ARUPS was performed [65-67].

2. Experimental

The experiment was performed using a VG-ADES-400 system, equipped with ARUPS, XPS and LEED units. The experimental configuration for ARUPS is shown in fig. 1. The energy resolution of the spectrometer was 0.1 eV for He I \( (h\nu = 21.2 \text{ eV}) \) and 0.25 eV for He II \( (h\nu = 40.8 \text{ eV}) \), and the angular resolution was 2°. The base pressure is \( 1 \times 10^{-10} \text{ Torr} \). In situ sample preparation was carried out in a separate chamber with a base pressure of \( 1 \times 10^{-9} \text{ Torr} \).

The MgO single crystal (99.98% pure, W&C. Spicer & Co. Ltd., UK) was cleaved in air along a \{100\} crystal plane. It was mounted in a stainless steel sample holder, which also makes electrical contact with the edges of the cleaved surface using a graphite coating. After introduction into the preparation and subsequently into the measuring chamber, the surface shows a clear and sharp \( 1 \times 1 \) LEED pattern at primary electron energies above 110 eV. Contaminants on the surface, found using XPS and ARUPS, were removed by 500 eV, 2 \( \mu \)A argon-ion bombardment for 20 min under a 45° angle of incidence. No degradation of the LEED pattern can be observed afterwards. Traces of CO, residing in the bulk material, can still be found in the photoemission spectra.

Charging effects were reduced by the use of the graphite contacts. A clear LEED pattern can be observed even for primary electrons with energies...
as low as 58 eV for several minutes. Charging effects due to light irradiation during ARUPS experiments were compensated using a flood-gun, spraying about 8 $\mu$A of electrons onto the sample holder with a maximum primary energy of 3 eV. This compensation was sufficient as evidenced by the fact that a factor of four variation of the HeI intensity by changing the He pressure in the discharge lamp, results in a proportional variation of the MgO valence band spectral intensity without a detectable shift in the energy positions of the peaks or broadening of the peaks. However, the He discharge pressure is kept at a minimum in order to minimize possible residual charging effects. This in addition made it possible to record the HeI and HeII spectra at the same discharge pressure, thereby eliminating possible differences in photoelectron kinetic energy scale due to differences in charging, if any. During measurements, no contamination from the tungsten filament of the flood-gun has been observed and the MgO(100) surface remained clean for at least 8 h. Several cycles of argon sputtering followed by a 6 h measurement were needed in collecting and reproducing the data for the emission angles required. Two samples were used, giving the same results.

All HeI and HeII spectra were corrected for the analyzer transmission, which was taken proportional to the reciprocal kinetic energy.

3. Results

We first investigate the effect of argon sputtering on the quality of the MgO(100) surface. Fig. 2 shows a HeI ($h\nu = 21.2$ eV) valence band spectrum at normal emission for a surface after 1 and 10 h of sputtering. Only some small changes can be noticed at about 16 eV kinetic energy, just above the top of the valence band, which might be attributed to surface defect states like in the case of NiO and TiO$_2$ [1,68,69]. The $1 \times 1$ LEED remains still clear and sharp. Degradation of the LEED can be noticed after 20 h of sputtering. The data presented below are collected from surfaces which have had less than 3 h of total sputtering time. A small feature at 17.4 eV kinetic energy can be noticed already for very little sputtering. To what extent this can be attributed to surface or bulk like defects is at the moment not clear. The small peak at 9 eV kinetic energy does not change in intensity as a function of sputtering time. A similar behaviour is shown by the small C 1s line in XPS. The correspondence indicates that this peak might be assigned to carbonate species residing inside the MgO bulk.

The results of ARUPS measurements using unpolarized HeI ($h\nu = 21.2$ eV) and HeII ($h\nu = 40.8$ eV) radiation are presented in figs. 3a, b and 4a, b, respectively. The photon angle of incidence ($\alpha$) is 15° with respect to the surface normal. The emitted electrons have been collected in the $\Gamma$XWK and $\Gamma$XUL planes of the first bulk Brillouin zone (1BBZ) at various polar angles ($\Theta$).

The HeI spectra (figs. 3a and 3b) reveal a MgO valence band which consists of a main peak at 14.0 ± 0.2 eV kinetic energy and a small peak at 11.5 ± 0.3 eV. No dispersion ($< 0.2$ eV) can be observed for the peaks as a function of emission angle. The peak at 9 eV, as mentioned above, can be assigned to carbonates in the bulk material.

The HeII spectra in the $\Gamma$XWK emission plane (fig. 4a) show two strong peaks at 34.7 ± 0.2 and 31.2 ± 0.2 eV kinetic energy. Some dispersion, about 0.5 eV, can be observed for the first peak at emission angles between 18° and 45°. Another
strong dispersive feature (marked by streaks in fig. 4a) can also be observed at emission angles between 0° and 21°, which looks quite broad due to the limited angle resolution of the spectrometer (2°). The peak at about 28 eV is due to the above-mentioned carbonates.

Similar features can be observed in the He II spectra in the ΓXUL emission plane (fig. 4b): two strong peaks at 34.6 and 31.2 eV, a 0.5 dispersion for the 34.6 eV peak between 12° and 45° emission angles and a strong dispersion for a broad peak (marked by streaks in fig. 4b) between 0° and 18°. In addition there is also a strong and sharp peak showing a 2 eV dispersion at emission
angles between 18° and 39°. We have investigated the dispersion of this peak in more detail as shown in fig. 5.

4. Discussion

The HeI spectra show very little angle dependence, in contrast to the HeII spectra where several strongly dispersive bands can be noticed. A similar phenomenon has been observed by Himpsel and Steinmann [65,66] in their work on photon energy dependent photoemission on NaCl. They found that for low photon energies the angular distribution does not depend on the initial state. They attributed this effect to the fact that the final energy of the electrons is below the electron–electron scattering threshold, which is
Fig. 5. Angle-resolved valence band spectra in the ΓXUL emission plane, using HeII (hv = 40.8 eV). The spectra have been corrected for analyzer transmission and normalized to the integrated valence band intensity.

Fig. 6. Schematic energy level diagram of the MgO/vacuum/spectrometer system. A photon with energy hv creates a photoelectron with initial state energy (E) which is given relative to the top of the valence band (E_v). The kinetic energy (E_{kin}) of the photoelectron is measured relative to the vacuum level (E_{vac}) at the spectrometer site. The difference between this vacuum level and the Fermi level (E_F) is the spectrometer workfunction (\phi = 4.4 eV). The vacuum level at the MgO site is raised by the flood-gun electron energy (V_{fg} = 3 eV). The energy difference between the top of the valence band (E_v) and the vacuum level at the MgO site is the ionization potential (IP = 9.1 eV). The energy difference between the bottom of the free-electron final states inside the MgO and the vacuum level at the MgO site is the inner potential (V_0 = 9 eV). Also shown is the energy gap (E_{gap} = 7.8 eV) between the top of the valence band and the bottom of the conduction band.
about 3 eV as shown in fig. 6, the kinetic energies at the MgO will be between 8 and 12 eV, which are all below the threshold. Therefore, angle-integrated transitions tend to dominate the He I ($h\nu = 21.2$ eV) spectra and direct bulk transitions might give an important contribution to the He II ($h\nu = 40.8$ eV) spectra. The fact that for low photon-electron kinetic energies, electron–electron scattering processes are strongly reduced and consequently the photoelectron escape depth is enhanced significantly, is also demonstrated by the fact that the He I photoemission intensity of MgO is about a factor of 10 to 20 larger than that of materials like Cu, Cu2O, CuO, Ag and Ag2O.

In analyzing the ARUPS data, we will make a comparison to results from available bulk band-structure calculations. Since these are only available along high symmetry lines in the Brillouin zone, we carry out a Slater–Koster [70] linear combination of atomic orbitals (LCAO) tight-binding calculation for the valence band, including only O 2p and Mg 3s orbitals for convenience. The parameters in this model calculation are found by fitting the results to those of the ab-initio pseudo-potential calculations by Chang and Cohen [56]. The resulting band-structure is shown in fig. 7 and the parameters used are $s_0 = 10.20$, $(ss\sigma)_2 = -0.20$, $(sp\sigma)_1 = -0.60$, $(sp\sigma)_2 = -0.30$, $p_0 = -1.84$, $(pp\sigma)_2 = 0.60$ and $(pp\pi)_2 = -0.07$ eV, where s and p denotes the Mg 3s and O 2p orbitals, respectively, and where the subscript refers to the order of nearest neighbors. The energy zero is set to the top of the valence band. The calculated total density of states (DOS) is shown in fig. 8.

The He I spectra, which show very little angle dependence, can be compared with the calculated total DOS (fig. 8). Two peaks can be seen in the

![Fig. 7. Bulk band-structure of MgO from the tight-binding fit to an ab-initio pseudo-potential calculation [56].](image)

![Fig. 8. Total DOS from the tight-binding model. A Lorentzian broadening of 1 eV has been included.](image)
total DOS, one at -0.9 eV and one at -3.6 eV. The energy separation of these two peaks (2.7 eV) corresponds quite well with that of the experimental peaks (2.5 eV). The experimental 14 and 11.5 eV (kinetic energy) peak positions can be matched to the calculated ones, if the experimental kinetic energy scale is shifted downward by 15.0 ± 0.2 eV. This would mean that the ionization potential (IP) of MgO is about 9.2 eV, calculated from $h\nu - 15.0 + V_{fg}$, where $h\nu$ is the photon energy (21.2 eV) and $V_{fg}$ the flood-gun electron energy (~3 eV). See also the energy level diagram in fig. 6.

In interpreting the HeII spectra, which show strong angle dependence, we make use of the conservation law for momentum parallel to the surface and calculate the initial state parallel momentum ($k_\parallel$) in the MgO according to

$$k_\parallel = \left(\frac{2mE_{\text{kin}}}{h^2}\right)^{1/2} \sin \theta,$$

where $m$ is the free-electron mass and $E_{\text{kin}}$ the electron kinetic energy outside the solid. We also make use of the direct bulk transition model. In order to calculate the initial momentum perpendicular to the surface ($k_\perp$), we assume free-electron-like final states in the solid, having an energy of $h^2k^2/2m^* - V_0$ relative to the vacuum level at the MgO or $h^2k^2/2m^* - V_0 + V_{fg}$ relative to the vacuum level at the spectrometer (see fig. 6). Here $V_0$ denotes the inner potential, $m^*$ the electron effective mass and $k^2 = k_\perp^2 + k_\parallel^2$. For a fixed final state energy we then find a set of ($k_\perp$, $k_\parallel$) points lying on a circle as shown in figs. 9a and 9b for the ΓXWK and ΓXUL emission planes respectively.

The peaks observed in the HeII spectra, in both the ΓXWK and ΓXUL emission planes, have kinetic energies lying between 31.2 and 34.6 eV at the spectrometer. Assuming an inner potential of about 9 eV (see below) and having a flood-gun electron energy of about 3 eV, we have to deal with free-electron states with energies between approximately 37.2 and 40.6 eV relative to the bottom of the free-electron bands. In comparing experiment with theory, we therefore consider circular sets of ($k_\perp$, $k_\parallel$) points with radii of 3.15 Å⁻¹ (dashed line, 37.8 eV) and 3.25 Å⁻¹ (solid line, 40.2 eV) in figs. 9a and 9b, assuming $m^* = m$. The band-structure along these “paths” in the bulk Brillouin zone can correspondingly be calculated as shown in figs. 10a and 10b. The energy positions of the peaks observed in the HeII spec-

Fig. 9. Free-electron final state energy contours in the (a) ΓXWK and (b) ΓXUL emission planes. The solid circle corresponds to an energy of 40.2 eV relative to the bottom of the free-electron band (radius 3.25 Å⁻¹) and the dashed circle to 37.8 eV (radius 3.15 Å⁻¹).
Fig. 10. Bulk band-structure of MgO along circular paths in the (a) ΓXWK and (b) ΓXUL planes as shown in figs. 9a and 9b, respectively. The solid line corresponds to a circular path with a radius of 3.25 Å⁻¹ and the dashed line to a circular path with a radius of 3.15 Å⁻¹. The energy positions of the peaks in the He II (hν = 40.8 eV) angle-resolved spectra in the ΓXWK (fig. 4a) and ΓXUL (figs. 4b and 5) planes are indicated by (○), after application of a downward shift of 34.7 eV.

tra are also included in these figures, where the experimental kinetic energy scale is shifted downward by 34.7 eV to match the calculated bands. This shift corresponds to an ionization potential (IP) of about hν - 34.7 + V₀ = 9.1 eV, consistent with the value found for the He I spectra.

Good agreement between theory and experiment can be seen for most of the points, especially in fig. 10b. This indicates that the assumptions of direct bulk transitions and free-electron-like final states are reasonable. It also justifies the choice of m* = m and V₀ = 9 eV. In fact, from the differences between the dashed and solid lines in fig. 10b one can deduce that the value for V₀ is not critical within 2 to 3 eV. Somewhat higher values for the inner potential have been used in LEED studies [11–15], they range from 10 up to 15 eV.

Deviations between experiment and theory in the ΓXUL emission plane (fig. 10b) occurs for experimental peaks at -3.4 eV for k∥ between 0 and 1 Å⁻¹. The same deviations can also be found in the ΓXWK plane (fig. 10a), where in addition peaks at -0.9 eV for k∥ between 1 and 2 Å⁻¹ are not reproduced by theory. The energy positions of these peaks however, corresponds quite well with the positions of the two peaks occurring in the calculated total DOS (-0.9 and -3.6 eV) as shown in fig. 8. This strongly suggest that also angle-integrated transitions contribute to the He II spectra.

Another way of analyzing the spectra is to assume that the initial electron momentum perpendicular to the surface (kₚ) is random, such that the spectra would be dominated by bulk one-dimensional density of states (OD-DOS) structures. Such an analysis is given in fig. 11, where the bulk-allowed states projected onto the (100) surface are given by the hatched area. Fig. 11 reveals that the dispersion of experimentally observed peaks in He II spectra is not compatible with the periodicity of the (100) surface Brillouin zone. This contradicts the OD-DOS model but supports the direct-transition model. However, the fact that also dispersionless features are seen, which correspond to a total DOS, suggests randomization of k (both kₚ and kₚ) perhaps due to phonons. It is interesting to note that the experimental peaks at the M point (fig. 11) fall outside
Fig. 11. Surface band-structure of the MgO(100) along $\Gamma\bar{M}$ and $\Gamma\bar{X}$ lines. The bulk projected OD-DOS is denoted by the hatched area. The energy positions of the peaks in the HeII ($h\nu = 40.8$ eV) angle-resolved spectra the $\Gamma\bar{X}WK$ (fig. 4a) and $\Gamma\bar{X}UL$ (figs. 4b and 5) planes are indicated by ($\bigcirc$), after application of a downward shift of 34.7 eV.

5. Conclusions

We show that the electronic structure of MgO can be studied using angle-resolved ultraviolet photoelectron spectroscopy. Charging effects have been managed by means of an electron flood-gun. Features in the spectra, taken from the MgO(100) surface, can be assigned to a superposition of angle-integrated bulk transitions and direct bulk transitions, the ratio of which depends on the final state energy of the photoelectrons and subsequently on the photon energy. The results are in accordance with ab-initio bulk band-structure calculations.

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