# Electronic band structure of calcium oxide

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Abstract. We have measured the bulk energy-momentum resolved valence band structure of calcium oxide by the means of electron momentum spectroscopy (EMS). We have extracted the band dispersions, bandwidths and inter-valance gap, electron momentum density (EMD) and density of occupied states (DOS) from the measured data. The experimental results are compared with theoretical band structure calculations performed within the full potential linear muffin-tin orbital (FP-LMTO) approximation. The valence band dispersions are in good general agreement with the theory, although small discrepancies exist. We have obtained  $0.63 \pm 0.15$  and  $1.2 \pm 0.1$  eV for the widths of the s-and p-subbands correspondingly. While the last number agrees well to the theoretical value of 2.6 eV after accounting for the experimental conditions, the former one suggests a slightly higher value compared to the theory. The measured intervalence gap of  $14.69 \pm 0.05$  eV is at odds with the theoretical prediction being larger as much as about 1.7 eV. However, the measured s-p subband splitting of 16 eV agrees well to the measurement of other researches. The experiment also reveals a significantly higher intensity of the *p*-subband compared to the *s*-subband than follows from the theory. We have also made measurements of the Ca 3s and 3p core levels. Their splitting of 18.7 eV is in excellent agreement with the literature data and their

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dispersions agree well to our previous theoretical calculations. However, the experiment gives the Ca 3p - s-subband splitting of 4.3 eV, which is higher of the available theoretical predictions.

### 1. Introduction

In the light of the rapidly increasing technological importance of alkaline-earth oxides the knowledge of their electronic properties is becoming vital to secure a successful advance in production of new materials on their basis. Such characteristics of alkaline-earth oxides like high mechanical and radiation resistance strengths, transparency in the infrared, visible and vacuum ultraviolet regions of the spectrum open a wide perspective for their application in high temperature technique, microelectronics and heterogeneous catalysis to mention a few. They are also of geophysical interest<sup>1</sup> because, particularly, MgO and CaO are present in significant amounts in the lower mantle of the Earth where pressure reaches up to 140 GPa. Their high-pressure behavior was the subject of several experimental (see, for example Richet *et al*<sup>2</sup>) and theoretical<sup>3</sup> studies.

The electronic structure of CaO that is an interesting representative of the alkalineearth oxide group is a subject of our paper. At normal conditions CaO crystallizes into the cubic rocksalt (NaCl) structure and is considered as a prototype oxide from the theoretical point of view. This compound exhibits properties typical of an insulator with a wide band gap of 7.7 eV<sup>4</sup> and also of a semiconductor with a large dielectric constant of 11.8.

In a simple ionic model CaO in a solid state is formed by an array of cations  $Ca^{2+}$  and anions  $O^{2-}$  with pure ionic bonding between them. Despite the obvious success of this model<sup>5</sup> it fails to correctly predict the band gap of this ionic solid. One of the reasons is some degree of covalency existing in the bonding. A competing picture is provided by a model postulating delocalization of one electron transferred from cation to anion  $(Ca^{2+}O^{-}$ plus e<sup>-</sup>)<sup>6,7</sup>. This model is maintained by two factors: (a) the low-lying empty 3*d* orbitals of the cation<sup>8</sup> and (b) the instability of the O<sup>2-</sup> ion due to not sufficiently strong Madelund potential<sup>9</sup>.

A number of band structure calculations on CaO have been done using various theoretical approaches<sup>10,11,12,13,14,15,16,17,18,19,20,21</sup>, but experimental investigations performed on this compound are quite limited. O'Bryan and Skinner<sup>22</sup> have measured the K-emission spectra of Ca using soft X-rays and obtained the first estimate of bandwidth of 15 eV for the upper valence subband. Several authors<sup>23,24,25</sup> have made XPS measurements of the valence band and Ca 3p and 3s semi-core levels. A few optical measurements were also performed on CaO to probe the conduction and valence band structures (see, for example Whited and Walker<sup>26</sup>). However, none of the above-mentioned experimental technique delivers the full energy-momentum resolved band structure, which is quite important for the accurate description of the electronic properties. Angle resolved photoemission spectroscopy (ARPES) could provide the full band structure information, but to our best knowledge there are no reported ARPES measurements of CaO.

To study the valence band and core-level structure of polycrystalline CaO films we are using electron momentum spectroscopy (EMS) that is proved to be successful in probing electron distribution in the energy-momentum space. During the past 30 years it has been applied to a variety of targets in gaseous<sup>27,28</sup> and solid<sup>29,30,31,32</sup> forms. EMS allows us to

directly observe the dispersion relation in bands and also measure band intensities, i.e. the full band structure of the target.

In this paper we report on the valence band and semi-core levels of Ca measured in CaO. The experimental results are compared to theoretical calculations in the full potential linear muffin-tin orbital (FP-LMTO) approximation and also to the results of other researches. This comparison is thought to serve as a sound basis of helping in a further elucidation of possible improvements in the theoretical description of such a useful reference system as CaO is. The paper is organized as follows: in the next section a description of our spectrometer is furnished followed by the target preparation and characterization. A short memo of the FT-LMTO method and theoretical results for crystalline CaO are given in section 3. Section 4 is dealing with the results of the experiment and theory and their comparison, followed by an account on the semi-core levels of Ca (3s and 3p) in section 5. Concluding remarks are presented in section 6.

# 2. Experimental technique

### 2.1. (e,2e) spectrometer

A somewhat detailed description of our spectrometer could be found in the literature<sup>33</sup>, here we limit themselves only to a few remarks on the principle of its operation and its main parameters. An alternative name of the spectrometer, (e,2e) spectrometer, implies that its operation is based upon the electron ionization impact reaction<sup>27,28,34</sup>, when an energetic incident electron knocks out an electron of a target with a subsequent detection of two outgoing electrons. In the case if a momentum transfer of the incident electron to the target is

high enough then the ionization event could be treated in the plane-wave impulse approximation. In this approximation the momentum q of the bound electron *before* the collision is equal and opposite to the recoil momentum p of the ion, i.e.  $q = -p = p_s + p_f - p_0$ . Here the symbols  $p_s$ ,  $p_f$  and  $p_0$  are referring to the momenta of two outgoing (index *s* stands for the slow and f – for the fast electron) and incident electrons, respectively. The binding energy  $\varepsilon$  of the bound electron are determined by the conservation law neglecting the recoil energy of the ion  $\varepsilon = E_0 - E_s - E_f$ , where the symbols  $E_s$ ,  $E_f$  and  $E_0$  denote the correspondent energies. In the independent particle approximation the (e,2e) cross section at high energy and momentum transfer is proportional to the modulus square of the target electron momentum space wavefunction  $|\emptyset(\varepsilon, q)|^{27,35}$ , i.e., the electron spectral momentum density (SMD). Thus the measurement of the (e,2e) cross section at different  $\varepsilon$  and q is a direct mapping of the SMD of the bound electrons in the target. For this reason this technique is more commonly referred to as electron momentum spectroscopy.

Figure 1(a) shows the scattering geometry of our (e,2e) spectrometer which is characterized by non-coplanar asymmetric kinematics. This geometry enables the detection of the target electrons whose momenta are directed along the *y*-axis. The incident and two outgoing electrons have nominally energies of 20.8, 19.6 and 1.2 keV correspondingly. The outgoing electrons are detected on the opposite side of the target from the incident beam. The detected electrons are acquired into the electrostatic energy analyzers at polar angles of 13.6° and 76° relative to the direction of the incident beam. The fast electron analyzer with a pass energy of 100 eV accepts electrons over  $\pm 6^{\circ}$  azimuthal angles relative to the *x*-*z* horizontal plane, and similarly the acceptance of the slow electron analyzer is  $\pm 18^{\circ}$  with a pass energy of 200 eV. The overall momentum detection range is about  $\pm 3.5$  a.u. The achieved spectrometer resolution is about 1 eV for energy and 0.15 a.u. for momentum. The electron energy analyzers also deliver the timing information on electron arrival using which allows recognize electrons originated from the same (e,2e) event and in this manner significantly suppress background from random electron pairs.

An important characteristic of our spectrometer is that it is most sensitive to the outermost 2 nm surface layer of the target as shown in figure 1(b) by shading. This is resulted from a small escape depth of the slow electrons and hence most electronic structure information comes predominantly from this area. This feature facilitates measurements of the targets prepared by evaporation onto a thin substrate, for instance, amorphous carbon film, without it contributing to the signal. (e,2e) events occurring deeper within the target (non-shaded area) contribute mainly to the background intensity. Thickness of solid targets to be measured successfully by our spectrometer must not exceed of about 10 nm, otherwise the background events due to multiple scattering in the target dominates over the useful (e,2e) signal destroying the quality of electronic structure information<sup>36</sup>.

### 2.2. Sample preparation and Characterization

We have followed the target preparation technique similar to the one that was used for  $MgO^{30}$ . The evaporation apparatus of a simple construction (resistively heated boat) is located in an evaporation chamber where the base pressure is maintained at a level of  $10^{-10}$  Torr. It deteriorates typically one order of magnitude during the process. In order to degas evaporating species and in this way minimize a possible contamination of the formed layer we have made several preliminary runs of evaporation. 99% pure calcium flakes were heated

in the boat of the evaporator and deposited onto annealed amorphous carbon (am-C) substrates (3 nm thick). The slow rate evaporation (about 0.2 nm/min.) was practiced in the  $10^{-6}$  Torr oxygen background to let a sufficient time for oxidation of the deposited Ca layer. The overall layer thickness and deposition rate is measured by means of a quartz crystal microbalance. The optimum thickness of the formed layer is determined on the basis of two conditions: to provide a complete coverage of the am-C substrate surface and to exceed the sensitivity depth (2 nm) of our spectrometer. They guarantee a considerable suppression of input from am-C into the measured density. It was found that a 3 nm thick CaO layer is satisfying the both conditions. The structural character of the formed CaO films is believed to be polycrystalline.

In figure 2 we compare a typical Auger spectrum taken for a pure Ca surface (a) to a spectrum measured for the as-prepared CaO target (b). The insets show the Ca  $M_{2,3}VV$  line energy region in detail. Let us note that the energy scale in the CaO spectrum is shifted by about 10 eV towards higher energies due to a charge built on the target by the Auger electron gun current<sup>37</sup>. For this reason we cannot determine precise peak positions in the CaO spectra. A clear transformation of the spectrum for pure Ca is occurring due to oxide formation. First of all, a prominent O KLL line at about 525 eV has appeared. Secondly, as the results of an electron charge transfer from Ca cations to oxygen anions the Auger transitions, which involve the valence electrons, i.e., the Ca  $M_{2,3}VV$  and  $L_{2,3}M_{2,3}VV$  lines, have been strongly dampened. This is particularly explicit present itself for the Ca  $M_{2,3}VV$  line. The shape of the four  $L_{2,3}M_{2,3}M_{2,3}$  lines in the energy range from 292 eV to 303 eV for the Ca spectrum is also in a drastic change due to the different chemical environment of Ca. It would be anticipated these lines are shifted of an order of 10 eV towards lower energies

compared to pure Ca, i.e., its average position is around 290 eV in accord with the literature data<sup>24</sup>.

There are no clear indications on the presence of any amount of carbon on the surface in the CaO spectrum. However, a small signal at around 265 eV (the literature value is 275 eV<sup>38</sup>) may hint on its minimal presence. Our EMS data show only a negligible input from the am-C substrate. The origin of small broad structures (marked by arrows) observed about 35 eV down in energy from the intense Ca  $L_2 _3M_2 _3M_2 _3$  and O KLL lines is thought to be due to a 35 eV energy loss of Auger electrons in CaO. The band structure calculations assign this loss to the interband transition between the valence and conduction bands (see, for example Mattheiss $^{39}$ ). The same energy loss feature is also visible in the pure Ca spectrum.

In order to understand energy loss structures present in our EMS data due to multiple scattering processes we have performed electron energy loss (EEL) measurement of the asprepared CaO target. In this measurement the incident beam energy is tuned to the energy of the fast (19.6 keV) or slow (1.2 keV) electron analyzer and the energy spectrum of the scattered electrons is recorded. The result is shown in figure 3(a) and 3(b) for the fast and slow electrons correspondingly. The both spectra are normalized at the elastic peak height at zero energy loss. The fast EEL spectrum is prepared using the combined statistics from several CaO targets of different thickness (from 3 to 10 nm). It facilitates the purpose of parameterization of energy loss features. There are three energy loss structures in the spectrum. A broad peak centered at about 22.5 eV is due to am-C bulk plasmon losses and the other two around 14 and 37 eV are probably originated from losses due to excitation of valence electrons to low lying conduction bands in the CaO layer. However, the free- $\dot{u}_{pl.}$  associated with the six electrons of the upper valence band electron plasma energy

(UVB) is about 17 eV, which is only 3 eV off the first CaO peak in our spectrum, and hence a possible plasma origin of the 14 eV peak. The slow EEL spectrum that measured using a 3 nm thick as-prepared CaO target shows these structures as well.

We have made a least square fit to the fast EEL intensity to obtain precise positions and widths of the energy loss features. The fitting function was a linear combination of three Gaussians and a second order polynom to approximate the smooth background. The only fixed parameter was the position of the am-C plasmon (22.5 eV). A solid line in figure 3(a) shows the result. The obtained parameters are  $13.7 \pm 0.1$  eV and  $1.7 \pm 0.3$  eV for the position and width (FWHM), respectively, of the first CaO energy loss peak. The correspondent values for the second CaO peak are  $36.6 \pm 0.2$  eV and  $4.5 \pm 0.5$  eV. Rudberg<sup>40,41</sup> studying inelastic scattering of electrons in 'aged' Ca films on silver and platinum substrates got similar energy loss peaks. The peak positions extracted from fig. 10 of the paper of Rudberg<sup>40</sup> and averaged between the two Ca deposits give values that are very close to ours, namely, 13.6 and 36.5 eV. Whited and Walker<sup>26</sup> obtained the energy-loss function – Im å <sup>-1</sup> of CaO from the reflectance spectra using Kramers-Kronig dispersion analysis. The function shows a large peak at 35 eV and three small peaks at about 14, 18 and 27 eV. The energy (14 eV) of the biggest peak of the three is close to our result.

# 3. LMTO calculations

The band structure and the electron momentum density were calculated using the fullpotential linear muffin-tin orbital (FP-LMTO) method as described in Kheifets *et al*<sup>42</sup>. The local density approximation was employed with the Janak–Moruzzi–Williams parameterization to the exchange–correlation functional. The experimental lattice parameter a=4.8105 Å was used according to Wyckoff <sup>43</sup>. The FCC unit cell of CaO has two nonequivalent atomic positions at (0,0,0) and (1/2, 1/2, 1/2) occupied by the calcium and oxygen atoms, respectively. The two non-overlapping muffin-tin spheres were placed at this positions. The muffin-tin radius was set to a/4 which is one half of the distance between the neighboring calcium atoms.

The calculated energy bands (top row) and electron momentum densities (bottom tow) of CaO in several high-symmetry directions are shown in figure 4. The energy plots are split in two sub-bands. The lower sub-band consists of four bands formed by the two oxygen  $2s^2$  valence electrons hybridized with the calcium  $3p^6$  semicore electrons. The upper sub-band comprises 3 bands resulting from hybridization of the oxygen  $3p^4$  and calcium  $2s^2$  valence states.

The electron momentum densities are plotted on the bottom panels of Fig. 4. with the same line styles as used for the energy bands. The dotted lines show the three lowest bands derived from the calcium  $3p^6$  semicore states, the thick solid line indicates the lower oxygen 2s band and the thin solid lines show the three upper *p*-bands. The momentum densities of the *p*-bands are zero at zero momentum and reaches their maxima at less than 1 *a.u.* of momentum. The momentum density of the *s*-band is maximum at zero momentum and drops down quickly as the momentum increases. However, the momentum density decreases nonmonotonically because of a strong hybridization with the calcium  $3p^6$  states. The local minimum of the *s*-momentum density almost coincides with the maximum of the *p*-momentum density.

### 4. Results and discussion

#### 4.1. Valence Band

The experimental energy-momentum resolved density of the valence band and two core levels of Ca (3s and 3p) in CaO is shown in figure 5(a) as a gray-scale plot, a higher density shown by a darker color. Energy is referenced to the vacuum level of the spectrometer. One can see typical for ionic solids structures at about 8 and 24 eV where predominantly 2p and 2s levels of oxygen ions form the upper and lower valence subband, respectively. The upper and lower subbands are separated by an intervalence band gap of about 14 eV. The upper band consists of two branches symmetrically located about the A point, which is characteristic to the p orbital with its maximum density off the  $\tilde{A}$  point. The lower band is typical to the s orbitals with its maximum at the  $\tilde{A}$  point. Thereafter for short we designate them as s- and p-subbands referring to the lower and upper band, respectively. At about 28 eV 3p core level of Ca is visible. It lies only 4 eV down the s-subband, which results in its strong hybridization with the valence band. Its partial delocalization manifests itself in a small but still noticeable dispersion in binding energy. For this reason sometimes this level is called as semi-core level. A blurred spot around 47 eV showing no energy dispersion is due to 3s core-level of Ca.

There is also additional intensity present outside the above-mentioned structures due to multiple scattering of (e,2e) electrons in the target. Elastic scattering mainly causes a smearing of intensity along the momentum axis while inelastic scattering is responsible for intensity distributed along the energy axis. The latter causes intense background intensity particularly well visible just below the 3p Ca level. Fortunately, CaO does not display any strong collective plasma oscillation that is evident from our EEL measurements. The 14 eV and 37 eV energy loss peaks are not intense enough to produce any peak-like features in the EMS data and so the existing background in the experiment data is primarily smooth.

A faint parabolic feature having its minimum superimposed onto the *s*-subband and spreading nearly to the *p*-subband is belonging to the  $\delta$ -valence band of am-C<sup>44</sup>. A much weaker intensity from the  $\delta$ -bands of am-C is superimposed onto the *p*-subband. However, this background intensity interferes mainly with the *s*-subband. Scaling our previous EMS measurements of valence band for am-C we have subtracted it from the measured intensity. The result is shown in figure 5(b). The am-C band intensity has been completely removed and an overall level of multiple scattering background has also been significantly reduced.

The binding energy profiles extracted from the color plot in figure 5(b) are shown in figure 6 in a 0.2 au step. Since the intensity is supposed to be symmetric relative to the  $\tilde{A}$  point we have summed the positive and negative momentum components. The momentum width of the profiles is 0.05 au and the momentum range up to 2.6 au is covered. We have also performed least square fits of all four peak by Gaussians and the results are presented by solid lines. The *s*-subband and Ca 3p lines overlap each other and we have fitted them jointly and two other lines, *p*-subband and Ca 3s, were fitted independently. In all cases the underlying background was fitted by a linear function. The purpose of this fitting procedure is to remove a smooth background for a proper comparison of the experimental and theoretical band intensities.

In figure 5(c) we show the result of our FP-LMTO calculation of CaO valence band structure after two major additional transformations. First of all, to account for the polycrystalline nature of the measured target we have made spherical averaging of the theoretical intensity over the irreducible edge of the first Brillouin zone. Secondly, a convolution with two Gaussians, FWHM of 1 eV and 0.15 au, has been made to simulate the effect of the spectrometer resolution. Besides, the binding energy referenced to the valence band top is shifted up by about 9 eV to match the experimental and theoretical s-subbands. One can conclude from the color plots that the experimental and theoretical valence band structures are qualitatively alike, although there are two substantial differences. The first difference is related to the relative intensity of the two subbands. For the experiment a visual intensity of the *p*-subband is much higher than that of the *s*-subband while the LMTO the situation is in a reverse. It is worthwhile to remark, however, that the theoretical result is free from the additional intensity due to multiple scattering. Nevertheless, it is implausible from our point of view that this factor could change significantly the relative intensity of two subbands. The second difference is the intervalence gap, which is as much as about 2 eV smaller in the theory than in experiment.

In figure 7 we compare the experimental and two sets of theoretical valence band binding energy profiles in a 0.2 au step. The momentum width and range are identical to those of figure 6. A thick solid line is showing the LMTO result of figure 5(c) and a thin solid line is the original LMTO calculation spherically averaged but convoluted only with a 0.2 eV Gaussian. A smooth background has been subtracted from the experimental profiles as explained above. Intensities and energies for all sets of data are matched for the *s*subband. Comparing the *s*-subband peaks of the experiment and theory one can say that the experiment produces at least two times broader lines than those predicted by the convoluted LMTO. The multiple scattering evidently is responsible for the broadening. However, peak heights follow close to each other up to about 0.8 au. At higher momenta peak heights are dropping in magnitude much slower for the experiment than for LMTO (see, for example the 1.0 au interval). This is a direct consequence of the elastic scattering when the intensity smearing along momentum occurs resulting in a more uniform intensity distribution. Due to this smearing one can observed the experimental intensity up to a momentum of 1.8 au.

As noted earlier the intervalence band gap in the experiment is larger as much as about 2 eV than that of the theory. For this reason there is an energy shift of the same magnitude in positions of the correspondent *p*-subband peaks. At the  $\tilde{A}$  point the LMTO calculation predicts no intensity, which is typical for *p*-like orbitals, but the experiment is showing an intense broad structure of a width of approximately of 2.5 eV with the height even slightly larger than that of the correspondent s-subband peak. Another interesting characteristic of the measured *p*-subband peaks is that their widths are nearly the same as momentum increases. Only the upper portions of those peaks show a noticeable change in shape and position while their bases are nearly unchangeable up to 1 au of momentum and then slowly decreasing in height. It looks like that the measured structures consist of two components. The first component is the unchanged band intensity and the second one is formed as a result of smearing of a portion of the real band intensity by elastic scattering. A proper Monte Carlo simulation of multiple scattering processes in the target could more precisely explain the influence of those processes on the measured intensity. Our previous EMS measurements of metal oxides<sup>30,45,46</sup> show that the effect of elastic scattering is

especially drastic for p-subbands where a maximum intensity is not at the  $\tilde{A}$  point. The experimental intensity is tailing up to a momentum of 2.6 au while the LMTO intensity effectively goes only up to 2 au.

#### 4.1.1. S-subband

The s-subband is predominantly derived from 2s oxygen orbitals. In order to extract dispersion relations we have performed least square fits of the top regions of band peaks by Gaussians with all three variable parameters in binding energy profiles similar to those in figure 7. The results are shown in figure 8(a). The dispersion curve for the convoluted LMTO data is slightly shifted upward in energy (about 0.1 eV) compared to figure 7 to give a better comparison with the experimental result. One can see that the experimental data disperses approximately from 24.1 eV at the à point to 23.5 eV at 0.6 au with the median position at 23.8 eV. In the 0.6 - 0.9 au momentum interval the dispersion points slightly drop with a following flattening at a level of about 23.9 eV up to 1.5 au. However, as could be seen from figure 8(b) where electron momentum densities (EMD) are presented that starting from a momentum 0.6 au and higher the elastic scattering is 'bringing' all increasing relative portion of EMD for this momentum region. For this reason one can properly compare the dispersions only inside the 0.6 au momentum interval. The LMTO curve disperses from about 24 at the à point to 23.6 eV at 0.6 au. At higher momenta it is basically flat. However, the dispersions agree well in the 0.6 au momentum interval.

The bandwidth being determined as a difference of the minimum (bottom) and maximum (top) of the correspondent dispersion curve is  $0.63 \pm 0.15$  eV and 0.41 eV for the experiment and convoluted LMTO calculation, respectively. The full bandwidth predicted

by the LMTO calculation is 0.45 eV, which is 0.04 eV less of that determined for the convoluted LMTO by the method stated above. The small shrinking of bandwidth is a result of the convolution with the spectrometer resolution. Any other broadening mechanisms, for instance multiple scattering, are expected to lead to extra shrinking. In order to somewhat imitate the effect of multiple scattering on the measured bandwidth we have made an additional energy and momentum convolution of the LMTO data. The parameters of this convolution were chosen in such a way that to obtain equal peak widths with the experiment for the momentum profiles, which determine the bandwidth, at the  $\tilde{A}$  point and 0.6 au in our case. The new LMTO bandwidth is occurred to be 0.36 eV, the experimental and theoretical bandwidth difference being of 0.27  $\pm$  0.15 eV. This suggests that the experimental bandwidth is slightly larger than that predicted by LMTO calculation.

The result of the intensity integration along energy (EMD) in the binding energy profiles over a momentum range of 2 au is shown in figure 8(b) for the experiment and theory. The both data sets are normalized to unity and show their maxims around the  $\tilde{A}$  point, typical for a *s*-like orbital. There is good agreement of the experiment and theory up to a momentum of 0.6 au following a quicker decrease of EMD for the theory. As noted above the experimental EMD above 0.6 au is strongly enhanced by elastic scattering and, say, at a momentum of 1 au exceeds by a factor of two the predicted LMTO density.

There is no experimental data on bandwidth of the *s*-subband since for example, in XPS measurements it coincides with a larger signal from Ca 3p-core level<sup>24,25</sup>. Theoretical calculations, for instance, of Stepanova and her coworkers<sup>11</sup> (a linear method of augmented plane waves) and of Daude *et al*<sup>12</sup> (a combined tight-binding and pseudopotential method)

give values of 0.6 and 0.7 eV, respectively, which close to our experimental result on the bandwidth.

## 4.1.2. P-subband

The *p*-subband is comprised of 3 topmost bands (see figure 4). It is essentially derived from 2p oxygen orbitals, but in contrast to the *s*-subband it is strongly hybridized with 4s orbitals of calcium cation.

We have extracted dispersions for the experiment and theory in a similar manner to the s-subband. The results are presented in figure 9(a). The energy is reference to the vacuum level of the spectrometer. The convoluted LMTO data is shifted in energy by approximately 7 eV to match the minimum of the experimental dispersion which is located at  $8.80 \pm 0.08$  eV and a momentum of 0.4 au. The experimental data disperse from approximately 7.6 to 8.8 eV whereas for the convoluted LMTO data the correspondent range spreads from about 7.1 to 8.8 eV. Above a momentum approximately of 1 au the experimental band is nearly flat and in this momentum range multiple scattering perverts the real dispersion behavior. While the theoretical data show some wave-like pattern with noticeable minims at about 1.7 and 2.5 au the experiment points display only one rather shallow dip at 1.7 au. Nevertheless, there is a good overall agreement of the experiment and theory throughout nearly the whole momentum range of 2.7 au except for two points of discrepancy. The first one is related to an approximately 0.1 au shift of the experimental parabola-like dispersion curve (up to 1 au) towards smaller moment compared to the theory. A similar shift but only for the high momentum branch we have observed for BeO<sup>46</sup>. The second discrepancy is the energy position of the A point. The theory after applying the

convolution predicts 0.5 eV binding energy lower for the Å point than that of the experiment. We think that this discrepancy is originated because of multiple scattering since after applying some additional convolution to the LMTO data to account for its effects the binding energy of this point is lowering becoming close to the experiment.

The full LMTO bandwidth of the *p*-subband is 2.6 eV. Bandwidths extracted from the data in figure 9(a) are 1.68 and  $1.2 \pm 0.1$  eV for the convoluted LMTO data and experiment, correspondingly. These values are determined as the energy difference in positions of the binding energy peaks at the  $\tilde{A}$  point and the band minimum around 0.5 au. The theory predicts that the top of the *p*-subband lies at the  $\tilde{A}$  point although with zero intensity (see figure 4). The convoluted LMTO data show that this is the case - at all other momenta the dispersion curve lies below of its  $\tilde{A}$  point value of about 7.1 eV. The situation with the experiment is alike. Despite the fact that the experimental intensity is substantially higher compared to the convoluted LMTO data at the  $\tilde{A}$  point (see EMDs in figure 8(b)) and mainly due to elastic scattering we consider that the top band could be determined at the  $\tilde{A}$ This assumption is based on a property of elastic scattering to smear intensity point. basically along the momentum axis. After applying an additional convolution to the theoretical data in a similar manner done for the s-subband to simulate the effects of multiple scattering the theoretical bandwidth is shrinking further to 1.10 eV. This value agrees within the error to the experiment. We can conclude that there is no contradiction between the LMTO prediction and our experiment concerning the bandwidth of the *p*-subband.

As for other experimental bandwidths measurements we are aware only about two results. From the work of Doveren and Verhoeven<sup>25</sup> one can obtain a value of 3-4 eV for the bandwidth and Fiermans *et al*<sup>24</sup> observed the three peak structure with a overall width of 9  $\pm$ 

0.5 eV. The former value is in much better agreement to our result. The majority of theoretical calculations predict a value within 2-3  $eV^{11,13,14,15,16,17,18,19,7,20,45}$ .

The experimental and theoretical EMDs extracted from the correspondent binding energy profiles are presented in figure 8(b). Both sets of data are normalized to unity. The experiment shows an intensity of about 0.6 at the  $\tilde{A}$  point, the analogous value for the convoluted LMTO data is only about 0.04. As was pointed earlier the observed difference is believed to be due to elastic scattering. A high momentum tail is about as much as a factor two more intense in the case of experiment. The experimental EMD maximizes at a momentum around 0.65 au whereas the theoretical maximum is shifted approximately by 0.2 au. Besides, the average momentum is smaller for the experiment (0.88 au) than that for the theory (0.94 au). This average momentum difference of 0.06 au is thought to be considerable and could not be produced solely by elastic scattering for such a *p*-subband structure because it tends to smear intensity symmetrically and leave the average momentum value unchangeable. However, only a Monte Carlo simulation of multiple scattering processes could do the correct answer about the observed average momentum mismatch.

We have also calculated the density of occupied states (DOS) for the experiment and theory by integrating peak intensities in correspondent momentum profiles that are not shown here. The results are presented in figure 9(c). A dashed line is related to the LMTO prediction spherically averaged and convoluted only with the 0.2 eV Gaussian. All three data sets are normalized to unity and the theoretical data are shifted in energy by approximately 7 eV to match the minimum of the experimental band. The theory predicts that the DOS splits into two peaks separated by about 0.7 eV. However, after convolution the DOS is transformed into a single asymmetric peak (a solid line) of a width of about 1.7 eV (FWHM).

The experimental DOS shows a similar asymmetric peak of a larger width (2.6 eV) centered at 7.8 eV. The measured *s-p* subband splitting is equal to 16 eV, which is in excellent agreement with XPS data from the work of Fiermans *et al*<sup>24</sup>.

The experiment shows a significantly higher intensity in the *p*-subband compared to the *s*-subband than the LMTO calculation predicts. This is illustrated in figure 9 where the *p*-to-*s* relative intensity is shown. Multiple scattering has significantly changed this quantity at around the  $\tilde{A}$  point where the theory predicts zero intensity for the *p*-subband while the experiment gives a value slightly over 1. In the momentum region from about 0.2 to 0.6 au where the influence of multiple scattering on intensity is limited the experimental relative intensity is changing from 1.5 to 3. The theoretical range of values for the same momentum interval is from 0.2 to 1. In the middle of the momentum interval (0.4 au) the experiment yields the relative intensity as higher as 5 of that of the LMTO prediction. At momenta higher of about 0.6 au multiple scattering is playing significant role in the intensity redistribution (first in the *s*- and then in *p*-subband) and this produces basically a flat ratio at a level of 3. A similar discrepancy of the relative intensity we observed earlier in the case of MgO<sup>30</sup> and BeO<sup>46</sup>.

### 4.2. Ca 3p and 3s core levels

The Ca 3p semi-core level shows a much smaller compared to the *p*-subband but still noticeable dispersion due to a significant size of Ca cations. In order to obtain the dispersion relation we have performed least square fits of the correspondent peaks in the binding energy profiles of figure 6. The result is shown in figure 11(a). The binding energy is referenced to

the vacuum level of the spectrometer. The band disperses from about 27.75 eV at the  $\tilde{A}$  point to 28.4 eV at 0.6 au resembling a shifted parabola that is characteristic of a *p*-like orbital. After reaching a top energy of 27.95 eV at 1.05 au the dispersion goes again down to 28.2 eV at 1.7 au. However, over a momentum of about 1.05 au there exists a significant input of elastically scattering intensity and the dispersion determination is not reliable.

The measured bandwidth as determined from figure 11(a) is  $0.67 \pm 0.1$  eV with the median energy of 28.1 eV. To compare the obtained bandwidth with available theoretical predictions we need to bear in mind a significant shrinking of the full theoretical bandwidth observed in the case of the *p*-subband (from 2.6 eV to 1.1 eV) after applying of the convolutions. Values calculated in our previous work<sup>45</sup> using different theoretical schemes are ranging from 1.05 to 1.79 eV and assuming the same band shrinking one can obtain the correspondent bandwidth range from 0.44 to 0.76 eV. Our experimental result is in good agreement with these theoretical values.

Our experimental Ca 3p - s-subband splitting is estimated as large as 4.3 eV. There is no measured data for this quantity in the literature except for an upper limit of 2 eV quoted by Fiermans *et al*<sup>24</sup>. From the calculation by a full potential self-consistent method of linearised augmented plane waves of Mehl and his coworkers<sup>21</sup> and Redinger and Schwarz<sup>13</sup> this splitting is about 2.7 eV, which is significantly less of our result.

The measured EMD is shown in figure 11(b). The data is normalized to unity. The EMD is very resembling the EMD obtained for the *p*-subband. In the case of core-level the maximum density is occurring at a higher momentum of 0.75 au and the average momentum is also higher (0.96 au). The  $\tilde{A}$  point density is about 0.6, which is close to the  $\tilde{A}$  point EMD

of the *p*-subband. As said above the origin of this non-zero density is thought to be mainly due to elastic scattering.

We have fitted 3*s* core level peaks in the binding energy profiles of figure 6 to obtain its dispersion. The result is shown in figure 12. The energy is referenced to the vacuum level of the spectrometer. The Ca 3*s* core level is showing a very small but not zero dispersion in energy. Our estimate of  $0.24 \pm 0.07$  eV is in good agreement with the theoretical calculation of Sashin *et al*<sup>45</sup>. An approximate momentum spread of this level is of 1 au, which deductible from the figure as a momentum from which the data start showing a tendency of binding energy increase.

The measured median energy is 46.8 eV, which gives the Ca 3s-3p splitting of 18.7 eV. Doveren and Verhoeven<sup>25</sup> obtained a close value of 18.8 eV measuring XPS energies of the correspondent core levels. Using the same method Demri and Muster<sup>23</sup> bring out the identical value of 18.8 eV.

The question arises if there is any difference of the Ca 3s-3p splitting compared to metallic Ca. We have also measured these two core levels for metallic Ca<sup>32</sup> and obtained a value of  $19.4 \pm 0.5$  eV. One can see that our splitting value within the experimental error is identical for the metallic and oxide phase of Ca, which is also in agreement with the findings of Doveren and Verhoeven<sup>25</sup>.

#### 4.3. Valence Band and Core Level Structure Diagram

Using the measured EMS data we can draw an electronic structure diagram of CaO showing widths and positions of the valence band and Ca 3*s* and 3*p* core-levels. Such a diagram is

shown in figure 13. The energy is referenced to the *p*-subband top of the LMTO calculation. Four top boxes represent *p*-subbands, lower ones – *s*-subbands for four different data sets and other two boxes are related to the experimental core-levels. The first data set (first column of boxes) is the LMTO calculation with a minimal energy convolution (0.2 eV), the second set is for the LMTO data convoluted with the spectrometer resolution. The third set is the additionally convoluted LMTO data to simulate the effects of multiple scattering. This data set is thought to serve as only a qualitative guide. We call this data set as extra-convoluted LMTO. The forth column stands for the experimental results. The experiment data is shifted to match the minimum of the *s*-subband of the experimental and convoluted LMTO data.

As can be seen from the diagram there is only one substantial discrepancy of the experiment and theory. The experimental value of the intervalence gap is as much as about 1.7 eV larger than that of the LMTO prediction. A similar increase of the experimental gap was observed in our previous measurements of MgO<sup>30</sup> and BeO<sup>46</sup>. The full width of the valence band calculated as the energy difference of the  $\tilde{A}$  points of the *s*- and *p*-subbands ( $\tilde{A}_1$ 

 $\tilde{A}_{15}$ ) is as large as 16.5 ± 0.2 eV. Taking into account a probable shrinking of the experimental width as much as 0.8 eV one would expect a corrected value of the full bandwidth to be 17.3 ± 0.2 eV. The LMTO gives a value of 15.21 eV, which is about 2 eV less than the corrected experimental value. Comparing this quantity with the results of our previous calculations<sup>45</sup> the value of 16.7 eV obtained in the B3-PW scheme<sup>47</sup> is the closest to the experiment.

## 5. Conclusions

We have reported on the full energy - momentum resolved electronic structure of the valence band and the Ca 3s and 3p core levels in calcium oxide measured using electron momentum spectroscopy. We have also compared our experimental results to the band structures calculated within the full potential linear muffin-tin orbital approximation and to other experimental and theoretical results.

Our experimental results on dispersion relations in the valence band show a good general agreement with the LMTO calculation. However, for the *p*-subband the experimental dispersion curve is shifted to a smaller momentum as much as 0.1 au compared to the theory prediction. This also results in a smaller average momentum for the experiment. The measured width of  $1.2 \pm 0.1$  eV agrees within the experimental uncertainty with the theoretical value of 2.6 eV after accounting for the spectrometer resolution and the effect of multiple scattering. The measured width of the *s*-subband of  $0.63 \pm 0.15$  eV is considered to be larger as much as  $0.27 \pm 0.15$  eV of the value predicted by theory (0.45 eV). The measured intervalence gap is larger as much as 1.7 eV than the LMTO predicts. However, the measured *s*-*p* subband splitting of 16 eV agrees well to the literature XPS data.

Electron momentum density for the *s*-subband determined from the experiment is in good accord with the theory up to a momentum of 0.6 au. At higher momenta the experimental density is higher as the result of multiple scattering the input of which is absent in the theoretical data. Multiple scattering is considered to be responsible also for the existing discrepancy for densities in the *p*-subband. This discrepancy is particularly apparent at the  $\tilde{A}$  point where the measured density is about of 0.6 with the zero prediction from the theory. The experiment also shows a considerably larger intensity in the *p*-subband to that of the *s*-subband compared to the theory. The size of this difference is significant and could not be explained by the effect of multiple scattering.

The measured dispersions for the Ca 3p and 3s core levels of  $0.67 \pm 0.1$  and  $0.24 \pm 0.07$  eV, respectively, are in good agreement with our previous calculations. The experimental Ca 3p – s-subband splitting is 4.3 eV, which is higher of available theoretical predictions. However, the measured Ca 3s-3p splitting of 18.7 eV is in excellent agreement with the data obtained by previous XPS experiments.

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# FIGURE CAPTIONS

**Figure 1.** Layout of (a) the scattering geometry, and (b) target orientation with respect to incident and two outgoing electrons. The shaded sectors of cones in (a) indicate the angular acceptance of two analyzers. The shaded layer in (b) represents the portion of the target that contributes most to measured spectral momentum density.

**Figure 2.** In (a) a typical Auger spectrum of a pure Ca surface and in (b) an Auger spectrum of a CaO surface formed by calcium deposition in the  $10^{-6}$  Torr oxygen atmosphere. Insets in the both pictures show a magnifying view of the Ca MVV line energy region.

**Figure 3.** Electron energy loss spectra of CaO targets on 3-nm thick am-C substrates (a) for the 19.6 keV electrons and (b) 1.2 keV electrons. In (a) a solid line shows the fit result of energy loss features.

**Figure 4.** Band dispersions (top row) and electron momentum densities for CaO calculated within the FP-LMTO approximation along several high symmetry directions.

**Figure 5.** Binding energy-momentum resolved densities in the valence band and Ca core levels of calcium oxide, (a) measured by EMS, (b) obtained from (a) after subtraction of the am-C input, (c) calculated within the FP-LMTO approach, spherically averaged and convoluted with the spectrometer energy and momentum resolution. The energy is referenced to the vacuum level of the spectrometer. The energy scale in (c) is shifted by

approximately 9 eV to match the minims of the *s*-subbands in (b) and (c). Density is depicted on a linear gray scale: darker color corresponds to higher density.

**Figure 6.** Experimental binding energy profiles for calcium oxide integrated over 0.05 a.u. momentum intervals in a 0.2 au step. Solid lines represent the results of least square fits to the valence band and Ca 3s and 3p core level peaks. The energy is referenced to the vacuum level of the spectrometer.

**Figure 7.** Background subtracted binding energy profiles for the valence band of calcium oxide integrated over 0.05 a.u. momentum intervals in a 0.2 au step from the experiment (points with error bars), the LMTO calculation convoluted with the spectrometer resolution (thick solid lines) and the LMTO calculation convoluted only with a 0.2 eV Gaussian (thin solid lines). Intensities of all data sets are normalized for the *s*-subband in the zero momentum profile. The energy is referenced to the vacuum level of the spectrometer. The energy scale for both LMTO curves is shifted by approximately 9 eV to match the minims of experimental and theoretical *s*-subbands.

**Figure 8.** In (a) *s*-subband dispersions and in (b) electron momentum densities (EMD) extracted from the binding energy profiles of the experiment (points with error bars) and the LMTO calculation convoluted with the spectrometer resolution (solid line) for calcium oxide. In (a) the energy is referenced to the vacuum level of the spectrometer. The LMTO curve is shifted by approximately 9 eV to approximately match the minimum of the *s*-subband in the experiment. In (b) both data sets are normalized to unity.

**Figure 9.** In (a) *p*-subband dispersions and in (b) electron momentum densities (EMD) extracted from the binding energy profiles from the experiment (points with error bars) and the LMTO calculation convoluted with the spectrometer resolution (solid line) for calcium oxide. In (c) density of occupied states (DOS) calculated from the momentum profiles from the experiment (points with error bars), the LMTO calculation convoluted with the spectrometer resolution (solid line) and the LMTO calculation convoluted with the spectrometer resolution (solid line) and the LMTO calculation convoluted only with a 0.2 eV Gaussian (dashed line). In (b) and (c) the experiment and LMTO data are normalized to unity. In (a) and (c) the energy is referenced to the vacuum level of the spectrometer and the LMTO curves are shifted by approximately 7 eV to match the minim of the *p*-subband in the experiment.

**Figure 10.** P - to - *s*-subband electron momentum density ratio for calcium oxide extracted from the binding energy profiles of the experiment (points with error bars) and the LMTO calculation convoluted with the spectrometer resolution (solid line) as a function of electron momentum.

**Figure 11.** In (a) Ca 3p core level dispersion and in (b) electron momentum densities (EMD) extracted from the binding energy profiles of the experiment for calcium oxide. In (a) the energy is referenced to the vacuum level of the spectrometer. In (b) density is normalized to unity.

**Figure 12.** Ca 3*s* core level dispersion extracted from the binding energy profiles of the experiment for calcium oxide. The energy is referenced to the vacuum level of the spectrometer.

**Figure 13.** Diagram of the valence band and Ca 3*s* and 3*p* core level structure of calcium oxide extracted from the LMTO ( $1^{st}$  column of shapes), the LMTO convoluted with the spectrometer resolution ( $2^{nd}$  column), the extra-convoluted LMTO (see the text for explanation) ( $3^{rd}$  column) and the experiment (the last column). Numbers in and under the shaded boxes indicate bandwidths. Errors are given in parenthesis for the last significant figures. The energy is referenced to the valence band top of the LMTO calculation. The energy scale of the experiment is shifted by approximately 9 eV to match the minims of the *s*-subbands of the experiment and convoluted LMTO.

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Fig. 1



Fig. 2





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Binding Energy (eV)

Intensity (arb. units)

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Fig. 8



Fig. 9

Fig. 10













