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The conduction bands of MgO, MgS and HfO₂

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Abstract. Electronic structure calculations for MgO, MgS and HfO₂ are reported. It is shown that the conduction bands of MgO and MgS have predominantly anion character, contrary to the common picture of the conduction band being derived from cation states. In transition metal oxides, unoccupied anion states are less important due to the presence of metal d states. The anion states are, however, still not negligible for a correct description of the conduction band, as will be shown for HfO₂.

1. Introduction

The alkaline-earth chalcogenides MgO and MgS are well-known compounds [1–4]. They are ionic insulators and crystallize in the NaCl structure. The valence band is formed by hybridized O 2p and S 3p states, respectively, while the bottom of the conduction band is commonly associated with Mg 3s states.

The latter is a rather intuitive interpretation of the conduction band based on the picture in which, when a crystal is formed by Mg atoms and either O or S atoms, the Mg 3s electrons are transferred to the chalcogen. We performed electronic structure calculations on MgO and MgS in order to reveal the origin of the conduction bands of these compounds. For comparison, the electronic structure of a transition metal oxide, HfO₂, is also calculated.

In the next section some details and a justification of the calculational methods are given. In section 3 the results of the calculations on MgO, MgS and HfO₂ will be discussed. In section 4 some concluding remarks will be made.

2. Methods

The electronic structures of all of the compounds considered here were calculated with the full-potential linearized augmented-plane-wave (LAPW) method [5]. In this method no approximations to the shape of the potential are made. The basis set contained approximately 250 (500) plane waves for MgO and MgS (HfO₂) and was extended with local orbitals for a better description of the semicore states. The Brillouin zone (BZ) integration was performed using the modified tetrahedron method on a special mesh of 72 (47) *k*-points in the irreducible part of the BZ of MgO and MgS (HfO₂). Experimental equilibrium unit-cell parameters were used in all cases.

In order to describe the conduction bands in terms of atomic wave functions, some calculations were performed with the localized spherical-wave (LSW) method [6]. In this method the potential is represented by spherically averaged potentials in overlapping space-filling spheres centred at the atomic nuclei (the atomic sphere approximation (ASA)). It

is known that within the ASA the electronic structure could be dependent on the specific choice of sphere radii. A thorough analysis of the influence of these parameters is made, providing both a justification of the ASA approximation and an insight into the failure of the ASA in cases where incomplete basis sets are used.

The basis sets were built from spherical Hankel functions, augmented in the spheres. The augmentation energies were chosen by solving the intra-atomic Schrödinger equation for each combination of quantum numbers n and l in each sphere (see the paper by Williams, Kübler and Gelatt on augmented-spherical-wave calculations [7]). These Hankel energies were calculated self-consistently, i.e. they were recalculated at the beginning of each iteration during the scf cycle. This procedure ensured that the augmentation energies were close to the band energies of interest, so the error due to the linearization process was small. Spherical Hankel functions with $nl = 3s, 3p, 3d$ were used for Mg, $3s, 2p, 3d$ for O, $4s, 3p, 3d$ for S and $6s, 6p, 5d$ for Hf.

Both the LAPW method and the LSW method are based on density functional theory, with the exchange–correlation energy treated within the local density approximation (LDA). It is known that the LDA suffers from a spurious self-interaction and that the LDA exchange–correlation energy lacks the required discontinuity at the Fermi energy. The main deficiency of the LDA for the compounds considered in this paper is a positioning of valence band states at too high energies, while the effects on the conduction bands are much less pronounced since these bands are unoccupied. As a consequence, the calculated band gaps are too small compared with experimental values, but an analysis of the conduction bands based on LDA calculations is justified.

Relativistic effects were included in the calculations except for the spin–orbit interaction. The neglect of spin–orbit interaction has some influence on the Hf 5d states in HfO₂. However, since the spin–orbit coupling of Hf 5d states is smaller than the energy difference between the bottom of the conduction band and unoccupied bands derived from other states, this will not influence the discussion on the origin of the conduction bands in this compound.

3. Results

In this section we will mainly discuss the electronic structure of MgO, which will be presented in section 3.1. It will be shown that the conduction band has primarily O 3s character. An analysis on the ASA approach will be given in section 3.1 as well. In section 3.2 we will show that the conduction band of MgS primarily originates from S 4s and S 3d states. To stress the difference in influence between alkaline-earth metals and transition metals on the conduction band in oxides, we will discuss the electronic structure of the transition metal oxide HfO₂ in section 3.3.

3.1. MgO

The oxide MgO [1–3] crystallizes in the NaCl structure with a lattice parameter $a = 4.2112 \text{ \AA}$ [8]. The band structure of MgO, calculated with the LAPW method, is shown in figure 1. The valence bands have a width of 5 eV and are primarily derived from O 2p states. The O 2s states, not shown in the figure, lie at 16 eV below the top of the valence band. Both the valence band maximum and the conduction band minimum lie at the centre of the BZ, so we predict a direct gap, which is in agreement with experiment. The size of the band gap is 4.7 eV, which is smaller than the experimentally determined value of 7.8 eV [2]. The underestimation of the band gap by a factor of roughly two is a common artefact of LDA calculations for these kinds of compound.

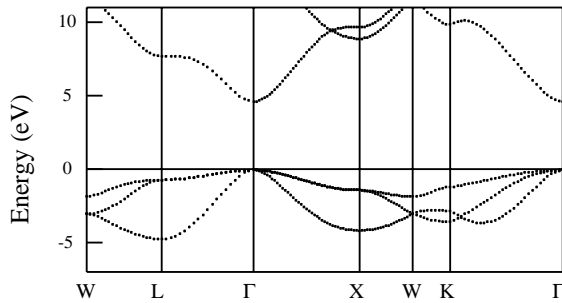


Figure 1. The band structure of MgO along some high-symmetry lines in the Brillouin zone, calculated with the LAPW method. The zero of energy is at the top of the valence band.

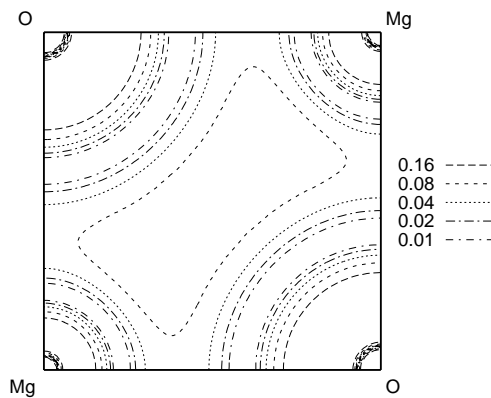


Figure 2. A contour plot in the (001) plane of the charge density (in atomic units) at the bottom of the conduction band of MgO.

The conduction band is a wide, rather free-electron-like band. Figure 2 shows a contour plot of the charge density of the wave function at the bottom of the conduction band in the (001) plane of MgO. The wave function is primarily centred at the O ions. The charge of this wave function is distributed among the O spheres (0.356 3s electrons per sphere), the interstitial space (0.516 electrons) and the Mg spheres (0.128 electrons per sphere). The sphere radii, chosen in the calculation, were 0.90 Å for Mg and 1.20 Å for O. The ratio of the chosen sphere radii, $r_{\text{O}}/r_{\text{Mg}} = 1.33$, is much smaller than the commonly accepted ratio of ionic radii [9], which is close to 2. Hence, the charge of the wave function at the bottom of the conduction band is primarily confined to the O ions.

In order to facilitate an analysis of the conduction band in terms of atomic-like wave functions, the band structure is also calculated with the LSW method. The band structure, calculated with the sphere radii $r_{\text{Mg}} = 1.15$ Å and $r_{\text{O}} = 1.43$ Å, is shown in figure 3. It shows a very good resemblance to the LAPW band structure in figure 1, although minor differences are visible at higher energies. This ensures the reliability of the ASA approximation.

Figure 4 shows again the LSW band structure of MgO, but now calculated without O 3s states. The band gap is indirect now and has increased to 9.4 eV, which is even larger than the experimental value. The direct gap at the Γ point is even 10.7 eV. The $r_{\text{O}}/r_{\text{Mg}}$ ratio of 1.24 in this calculation was also relatively small [9]. The fact that the presence

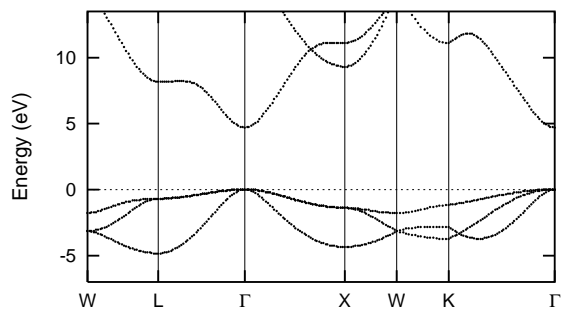


Figure 3. The band structure of MgO, calculated with the LSW method.

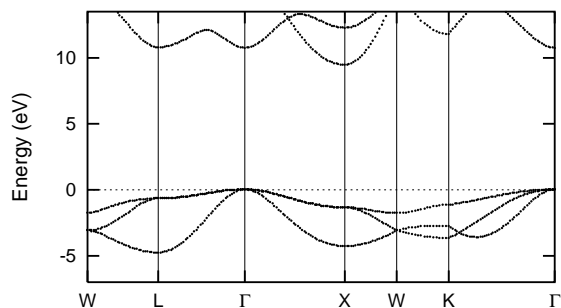


Figure 4. Like figure 3, but O 3s states were neglected in the calculation.

of O 3s states still has a strong influence on the band structure shows that O 3s states are very important for a correct description of the conduction band. If the O 3s states lay much higher in energy they would not have much influence on the band structure when neglected.

Determining the wave-function character of a delocalized band in terms of atomic wave functions encounters some difficulties. Several criteria can be used in order to judge with which atom a particular wave function or band should be associated. Among the theoretical criteria are the charge density, the integrated charges within specific volumes, the sensitivity of the band structure to the absence of specific basis functions, overlap integrals with specific basis functions and a cation- or anion-free band structure (see, for instance, section 3.2). From the experimental point of view, the measurement of electron–nuclear double-resonance (ENDOR) spectra, which determines the wave-function character at the atomic nuclei, is an important tool. The question arises of whether it is useful to assign atomic states to a free-electron-like band at all. If one insists on doing so, the lowest conduction band of MgO should be associated with O 3s states. This is especially important in electronic structure calculations. Unoccupied anion s states are not always included in calculations based on the ASA approach, while, for instance, quantum mechanical cluster methods are often not able to include those states at all.

The oxygen character of the conduction band has an interesting consequence in ASA calculations. Within the ASA one has the freedom to choose the sphere radii. Table 1 shows the band gap of MgO, calculated for a wide range of sphere radii, with and without the inclusion of O 3s states in the basis set. When those states are taken into account, the size of the band gap is not very dependent on the choice of sphere radii. Within the wide range considered here, the deviation from the accurate LAPW value is always smaller than ten per cent. Such differences are not unusual when comparing different methods.

Table 1. Direct band gaps of MgO at the Γ point as a function of the sphere radii, calculated with the LSW method. The first two columns list the radii of the Mg and O spheres. The other two columns show the band gaps, calculated with and without the inclusion of O 3s states in the basis set.

Radii (\AA)		Gap (eV)	
r_{Mg}	r_{O}	O 3s	No O 3s
0.79	1.58	4.2	15.4
1.15	1.43	4.7	10.7
1.31	1.31	5.1	6.9
1.43	1.15	4.4	5.4

When the O 3s states are not taken into account, however, the size of the band gap is not merely too large compared with the LAPW gap, but it also depends very much on the choice of sphere radii. Also the topology of the conduction bands changes considerably when the radii are varied, the band gap becoming indirect for very large O radii.

These results can be explained as follows. The conduction band has a predominant O 3s character. When O 3s states are neglected, i.e. the calculations are performed with an incomplete basis set, the conduction band cannot be correctly described with the available basis functions. Due to their rather delocalized character however, the states at the bottom of the conduction band can to some extent be described by Mg states by taking a very large, unphysical, radius for the Mg spheres. On the other hand, the error is largest for the largest O radii. Hence, the size of the deviation from the correct band structure is very dependent on the sphere radii if an incomplete basis set is used.

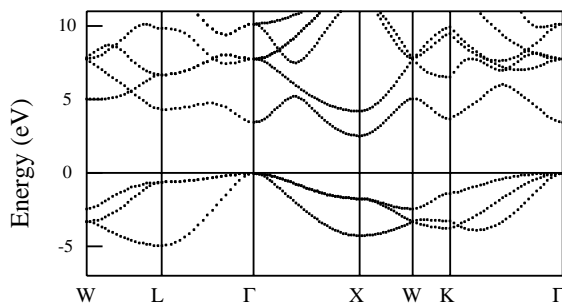


Figure 5. The band structure of MgS, calculated with the LAPW method.

3.2. MgS

The sulphide MgS crystallizes in the NaCl structure as well, but the lattice parameter is larger ($a = 5.2033 \text{ \AA}$ [8]) due to the large anion. The band structure, calculated with the LAPW method, is shown in figure 5. The S 3s states, not shown, lie at 11–13 eV below the top of the valence band, which is formed by hybridized S 3p states. The conduction band minimum is positioned at the X point in the BZ, leading to an indirect band gap of 2.6 eV. The direct gap at Γ is 3.5 eV. Experimental data are not available, but the prediction of an indirect band gap is in agreement with previous calculations [3, 4].

The wave function of the lowest conduction band at Γ has predominant S 4s character, in analogy to the O 3s character of the conduction band minimum of MgO. The wave

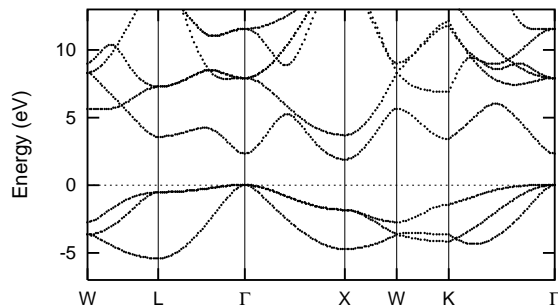


Figure 6. The band structure of a fcc lattice of S^{2-} ions with the same lattice parameter as MgS. Shown here are the S 3p, S 4s and S 3d bands.

function at the bottom of the conduction band, at X, has a strong contribution from S 3d states.

The sulphur character of the conduction bands is most convincingly shown by figure 6. This figure shows the band structure of a hypothetical fcc lattice of S^{2-} ions, which can be seen as MgS with the Mg^{2+} ions taken out altogether. The resemblance with the band structure of MgS itself is striking. Both the valence bands and the conduction bands are almost identical, which shows that there is almost no influence of Mg states in this energy region. The role of the Mg ions is therefore primarily that of stabilizing MgS in its existing structure.

3.3. HfO_2

The electronic structure of HfO_2 [10] was calculated for the fcc phase of HfO_2 with the lattice parameter $a = 5.115 \text{ \AA}$ [8]. The fcc structure is a high-temperature phase of HfO_2 , the low-temperature phase having monoclinic symmetry. The monoclinic structure, however, is just a small distortion of the high-symmetry fcc structure. Since the purpose of this paper is to give insight into the predominant factors determining the wave-function character of the conduction band of chalcogenides, we will merely discuss the simpler fcc phase.

Fcc HfO_2 has the CaF_2 crystal structure. It can be seen as a simple cubic lattice of O atoms with half the lattice parameter of HfO_2 , while half of the O cubes are filled with an Hf atom and the other half are empty.

The band structure of HfO_2 is shown in figure 7. The semicore O 2s and Hf 4f states,

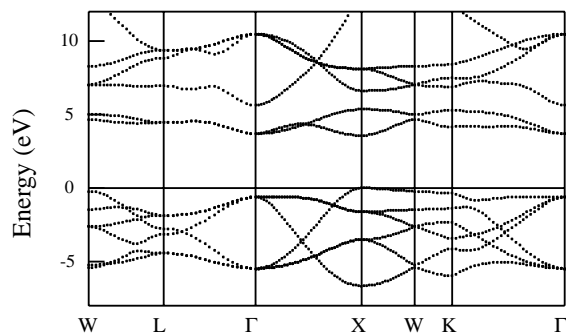


Figure 7. The band structure of fcc HfO_2 , calculated with the LAPW method.

which lie at 16–18 eV and 11.5 eV, respectively, below the top of the valence band are not shown. The valence bands, formed by hybridized O 2p states, have a width of 6.5 eV. The band gap, which is 3.6 eV, is direct since both the valence band maximum and the conduction band minimum lie at the X point.

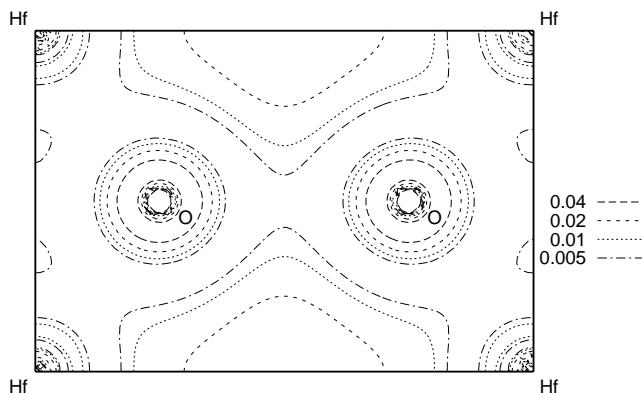


Figure 8. A contour plot of the charge density of the wave function at the Γ point of HfO₂, with an energy of 5.6 eV above the top of the valence band. Shown here is the (110) plane which intersects both Hf and O atoms as well as the empty positions at the centres of the oxygen cubes.

The two lowest conduction bands are primarily derived from Hf 5d (e_g) states. The Hf 5d (t_{2g}) states form three bands between 6 and 10 eV above the top of the valence band. There is one other band in this region, which is rather dispersive in the direction ΓX . This band can be identified as an O 3s band. The charge density of this band at the Γ point (energy 5.6 eV) is shown in figure 8. It is clear that a major part of the charge is confined to the oxygen atoms which lie in the middle of the figure. A substantial part of the charge is positioned at the centres of the oxygen cubes which lie at the middle of both the top and the bottom line of the figure. As is the case in MgO and MgS, the unoccupied cation s states lie at much higher energies.

4. Conclusions

The conduction band of MgO and MgS has a predominant anion character. In MgO the bottom of the conduction band is positioned at the Γ point and originates primarily from O 3s states. Due to the presence of S 3d states the bottom of the conduction band of MgS lies at the X point in the BZ, while the lowest conduction band at Γ has mainly S 4s character. These results are contrary to the common picture of the conduction band in alkaline-earth chalcogenides being primarily derived from cation states. Former calculations did not reveal the origin of the conduction band either since the results were not well analysed, or since unoccupied anion states were not even included in the basis set.

Unoccupied anion states are less important for the conduction bands in transition metal oxides, as we have shown for HfO₂. The lower conduction bands are primarily derived from metal d states, although the O 3s states still lie below the unoccupied metal s states.

It has recently been shown that the conduction band in alkali halides has a predominant anion character as well [11]. The alkali halides are strongly related to the alkaline-earth chalcogenides. MgO and MgS and almost all alkali halides exist in the NaCl crystal structure. Furthermore, they all are ionic insulators with a completely filled valence band

derived from anion p states. The main difference is in the charge of the ions, which is either +1 or -1 for the alkali halides, while the ions in alkaline-earth chalcogenides have charges of either +2 or -2. The results in this paper show that the conduction bands of the two categories are also similar, i.e. for both classes of compounds they are primarily derived from anion states as well. Furthermore, it is worthy of mention that MgH₂ also has valence and conduction bands which are both determined by the anions [12].

The peculiar property of the ASA approach, that the band gap of ionic insulators is sometimes strongly dependent on the sphere radii chosen in the calculation, is clarified in this paper as well. We have shown that in the case of MgO this effect can be addressed by the use of an incomplete basis set. When enough variational freedom is taken into account in the energy region of the conduction bands, the strong dependence of the band gap on the sphere radii is not found.

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