

SELF-CONSISTENT ELECTRONIC STRUCTURES OF MgO AND SrO

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The LMTO-method is used to calculate the band structure of the alkaline-earth oxides MgO and SrO. The cohesive energy and equilibrium lattice constant are also calculated. The results are compared with experiments and other theoretical calculations.

1. INTRODUCTION

MgO AND SrO REPRESENT two II–IV compounds crystallizing in the rocksalt structure with insulating characteristics, such as large band gaps, as well as semi-conducting (large valence band widths). MgO has been the subject of some parameter-free self-consistent band structure calculations [1–5], but for SrO there exists to the authors' knowledge only one such calculation [6]. The two compounds have, as should be expected, many similarities. But since the lowest lying unoccupied atomic orbital for the free Sr atom is of *d*-type and the one for the free Mg atom is of *p*-type we get some differences in the lowest lying conduction bands as we shall see.

The simplest qualitative picture of the electronic structure of the two compounds can be obtained by treating only the oxygen *2p*, the magnesium *3s*, and the strontium *5s* electrons as valence electrons, and considering all other occupied states as "core-states". The two valence *s* electrons of Mg or Sr are in this simplest picture used to fill the oxygen *2p* shell. The fact that we in our calculations do find the valence bands to be mainly of oxygen *p* character can be taken as a qualitative confirmation of parts of this model. But the valence bands are not of pure oxygen *p* type, and in fact our calculations indicate that, using an ionic picture, the compounds look more like Mg(+)*0*(–) and Sr(+)*0*(–) than like Mg(+ +)*0*(– –) and Sr(+ +)*0*(– –). However, the results supporting the Sr(+)*0*(–) and Mg(+)*0*(–) picture rely on values obtained from integrated charge densities. These quantities depend on the choice of dividing space into "metal" and "oxygen" regions, and they may be misleading as discussed in [4].

Within this simple picture the lowest lying conduc-

tion bands will mainly be of Mg *s*-type for MgO and of Sr *s*-type for SrO. And since *s*-bands have their minima at Γ , and the *p*-bands their maxima at Γ , the compound will be an insulator (or semiconductor) with a direct gap at Γ . We actually find that this qualitative picture concerning the nature of the gap holds for MgO (this is already known from previous calculations performed by other investigators), but it does not hold for SrO.

We have performed self-consistent Linear Muffin Tin Orbital (LMTO) calculations [7] with the Local Density Approximation of von Barth and Hedin [8]. The energy bands and the cohesive energy have been evaluated for the experimental lattice parameter. Calculations were also performed for varying the lattice constant around equilibrium for each compound. These calculations furnish the curve pressure versus lattice-constant from which the theoretical equilibrium volume V_0 , [$P(V_0) = 0$], and the bulk-modulus $B = -\partial P/\partial \ln V(V_0)$ are obtained.

X-ray Photoelectron Spectroscopy (XPS) can be used to give informations about the Density Of States (DOS) for the occupied states although the detailed structure of an XPS spectrum and in particular the intensity of the peaks, depends on the oscillator strengths (see for example [9]). The optical transition rates were not calculated here, but we assume that the spectral positions of the XPS-peaks correspond to those of the total density of states.

The density-of-states is decomposed into angular-momentum components, and the character (*s, p, d, . . .*) of a peak may be directly compared with experiments.

We shall now consider the results for each compound separately.

MgO

The MgO–SCF band structure along some high-symmetry lines in Brillouin zone are shown in Fig. 1. These bands correspond to the experimental lattice constant. The oxygens *2s* and *2p*, and the magnesium *3s* states were treated as valence states, all the other

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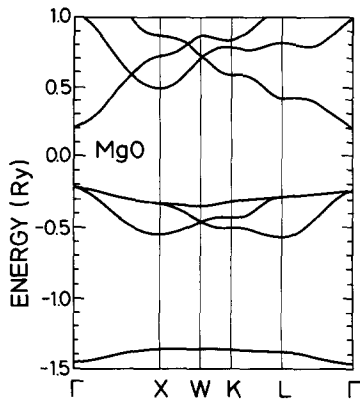


Fig. 1. Band structure of MgO. Scalar relativistic (i.e. spin-orbit coupling not included).

occupied states were regarded as renormalized, "frozen-core" states. In Fig. 1 we see some deep lying bands (semi-core states) arising mainly from the O-2s state. Above those we find the valence bands which come mainly from the O-2p states. The bottom of the conduction band is at the Γ point and it has an almost pure Mg-3s character. These results confirm the qualitative picture outlined in the introduction.

Kowalczyk *et al.* [10] have applied XPS in obtaining DOS curves for both MgO and SrO, and report results for core-, semi-core-, and valence states. In Fig. 2 we

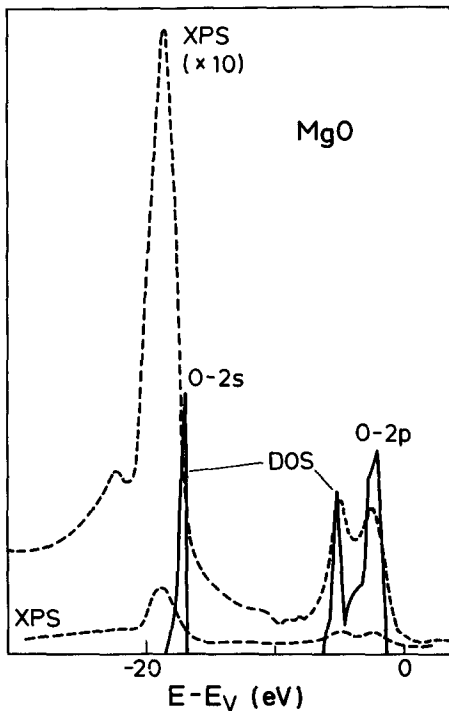


Fig. 2. Total density of states for MgO and XPS-spectrum [9].

show the DOS curves obtained for the valence states together with the XPS spectrum of [10].

For MgO our calculated DOS shows essentially three pronounced peaks: a low lying one from the semi-core O-2s states and two from the valence O-2p states. The separation between the p- and s-states is 13.5 eV which is in good agreement with the experimental value of 14 eV obtained in [10]. Furthermore, the separation between the two groups of O-p states is calculated to be 2.7 eV whereas XPS gives 2.5 eV.

The local density approximation is known to underestimate the gap of an insulator or semiconductor [11, 12]. Therefore, we expect, just like in the APW calculation of [4], and the pseudopotential calculation of [5], to underestimate the gap. The Hartree-Fock calculation, improved with addition of some correlation effects of [1] overestimates the gap somewhat. The Hartree-Fock-Slater ($X-\alpha$) calculations of [2] and [3] can give reasonable values of the gap depending on the choice of the α -parameter. Finally, the empirical methods of [13] and [14], and the semiempirical method of [15] are forced to give reasonable answers for the value of the gap and the valence-band width due to the adjustment to experimental data. The theoretical valence band widths are all of similar magnitude except for those of [1] and [15]. Due to imperfections, surface effects, etc. We would expect the largest experimental value [16] (8.54 eV) to be slightly overestimated. Our theoretical estimate of the equilibrium lattice constant is within 2.8% of the experimental value. The calculated cohesive energy, however, is considerably smaller than the measured [7] value (see footnote to Table 1).

In Table 1 we have collected different properties obtained in the present work, in other theoretical works, and in experiments.

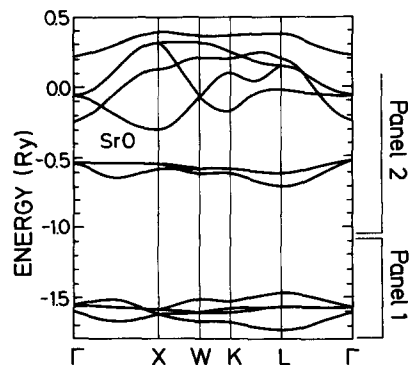


Fig. 3. Scalar relativistic (i.e. no spin-orbit coupling) LMTO band structure of SrO. The calculation was carried out using two energy panels (indicating on the figure), i.e. in each iteration two LMTO band-structure calculations were performed.

Table 1. Physical properties of MgO. The theoretical cohesive energy includes the atomic oxygen spin-polarization energy ($0.104 \text{ Ry/atom} \simeq 32.4 \text{ kcal mol}^{-1}$)

MgO	This work	Experimental works	Other theoret. works
Coh. energy (kcal mol^{-1})	246 [†]	725 [18]	267 [26] 700 [27] 650 [1] 660 [28] 650 [2] 228 [5]
Lattice const. (Å)	4.09	4.21 [19]	4.22 [26] 4.33 [27] 4.64 [1] 4.48 [28] 4.29 [2] 4.19 [5]
$B(10^{11} \text{ dyn cm}^{-2})$	17.1*	16.8 [20] 15.3 [21, 22] 16.0 [23]	17.08 [26] 19.5 [27] 16.2 [1] 18.3 [28] 24.1 [2] 14.4 [5] 4.69 [26]
Valence-band width (eV)	4.44	8.54 [16] 6.5 [10]	7.0 [1] 4.08 [2] 8.52 [15] 4.66 [4] 4.80 [5]
Band gap (eV)	6.06	7.8 [24, 25, 29]	8.9 [1] 5.37 [2] 7.76 [15] 8.15 [13] 7.77 [14] 7.53 [3] 4.45 [11] 4.50 [5]

* The bulk modulus was calculated using the experimental value of the lattice parameter.

† We have considered dissociation into neutral atoms and not into ions as sometimes done.

SrO

The strontium oxide has been far less studied, theoretically as well as experimentally, than the MgO. The SrO-SCF bands (scalar relativistic) are displayed in Fig. 3. The O-2s and -2p and the Sr-4s, -4p, and -5s are treated as valence states. The remaining states are treated as "frozen-core" states. The LMTO calculation was carried out using two energy "panels". As in the case of MgO, we observe some deep lying (semi-core) bands. However, in SrO these bands come from the hybridization of the O-2s and Sr-4p states. Consequently, semi-core peaks in the DOS-curve have a more complex structure.

The valence bands are mainly of O-2p type and a two-peak DOS-structure is found as in the case of the MgO. Unfortunately, Kowalczyk *et al.* [10] did not obtain any good results for the O-2p valence states for SrO. Therefore, no quantitative results were given [10] for the separation between the peaks in the XPS curve. Our calculation predicts (see Fig. 4) a two-peak O-2p structure with a value of the order of 1.0 eV for the separation of the peaks. The conduction bands are mainly formed from the Sr-5s and -4d states. The free Sr atom has unoccupied 4d states only slightly above the occupied 5s states. In the solid, these 4d and

Table 2. Physical properties of SrO.

SrO	This work	Experimental works	Other theor. works
Coh. energy (kcal mol ⁻¹)	221 ^{a,d} 227 ^{b,d}		
Lattice const. (Å)	5.22 ^a	5.16 [19]	
B (10 ¹¹ dyn cm ⁻²)	10.7 ^{a,c}		
Band width (eV)	2.38 ^b		1.72 [6]
Direct band gap (Γ) (eV)	4.26 ^b	5.90 [29]	3.90 [6]
Indirect band gap (eV)	3.83 ^b		

^a O-2s and Sr-4p treated as "frozen-core" states.

^b O-2s and Sr-4p relaxed, i.e. treated as band states (2-panel calculation).

^c The bulk modulus was calculated using the experimental value of the lattice parameter.

^d See footnote to Table 1.

5s states hybridize and produce low-lying conduction states with large *d*-components in particular at the *X*-point. The lowest lying conduction band from these *s-d*-hybrids has its minimum at the *X*-point causing SrO to be an insulator with an indirect Γ -*X* gap. This nature of the gap in SrO is similar to that of CaO where the lowest unoccupied orbitals of Ca are also of *d*-type. Results for CaO and BaO will be reported elsewhere [17].

Our calculations predict a value of 5.22 Å for the lattice parameter, which agrees with the experimental value of 5.16 [18] within 1%.

In Table 2 we have collected different properties obtained in the present work.

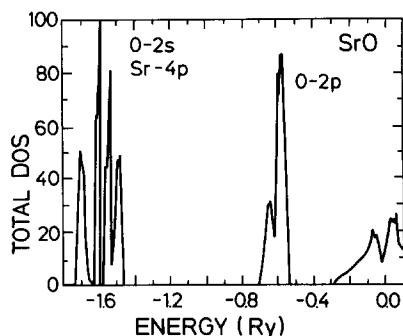


Fig. 4. Density of states (in electrons/cell/Ry) of SrO obtained from self-consistent fully relativistic LMTO calculations, i.e. spin-orbit coupling is included. The Sr-4s, -4p, -5s, and O-2s, -2p states are all treated as band states. The low-lying Sr-4s peak is not shown in the figure.

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