The nature of electron states in AlN and α-Al$_2$O$_3$

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Abstract
Both α-alumina and aluminium nitride are insulators. They are widely applied
as tunnel barriers. On the basis of first-principles calculations, it is shown
here that the conduction band of these two compounds is of fundamentally
different origin than generally assumed. The bottom of the conduction band
of both compounds is primarily derived from oxygen/nitrogen 3s states with an
admixture of a small amount of aluminium s character only. The presence of
the anion 3s states is of importance for the size of the band gap: without them
they would be significantly larger. The consequences of these differences are
discussed.

Aluminium oxide is applied in electronic tunnelling junctions [1, 2], initially in superconductor
junctions [2, 3], and recently in tunnelling devices with spin-polarized electrons [3–7]. The
understanding of these applications requires understanding of the electronic structure of the
individual components. Experiments show that α-Al$_2$O$_3$ is a wide-gap insulator with a direct
energy gap of about 8.3 eV at Γ [8, 9], larger than that of AlN (6.3 eV) [10]. Many theoretical
calculations have been performed for α-Al$_2$O$_3$ [8, 11–16]. The O–Al bonds in the compound
exhibit highly ionic nature [13, 17]. The valence band (VB) is well separated into two parts,
with the lower part consisting of O 2s states and the upper part being dominated by O 2p states.
The lower part of the conduction band (CB) is in general believed to be dominated by Al 3s
states [8, 11–17].

Recently, de Boer and de Groot revealed that for simple ionic crystals, e.g. for alkaline
halides, *both* the valence band and the bottom of the conduction band are determined by the
anions [18, 19]. The role of the cations is merely to provide the electron to fill the valence band
and to stabilize the crystal structure. This unconventional picture is confirmed by the invariance
of the size of the band gaps of alkali halides (the band gap is in first approximation determined
by the anion only; the influence of the metal is small and indirect through its influence on the
lattice parameter) and the topology of the band gaps (a metal-derived conduction band would
lead to an indirect band gap here, contrary to what is observed in experiments) [18, 19]. The
picture is not in contradiction with an ionic model, but it does imply that the band gaps of the
alkali halides are *not* of the charge-transfer type.

Since the oxygen–aluminium bond is of high ionicity in nature, it is timely to investigate the wave characters of the conducting electrons which not only dominate the tunnelling process in the spintronics [20], but also play an important role in alumina-based catalysis [21], the optical properties of F-centres [22, 23], etc. A second question we address here is to what extent anion-derived conduction bands in ionic compounds occur. Besides the I–VII alkali halides [18, 19], II–VI main-group metal oxides and sulphides show anion-derived conduction bands [24]. On the other hand, the conduction bands of III–V semiconductors have a pronounced metal character, as is already evident from the strong influence of the metal on size of the band gaps [18]. For this reason we also report results for AlN here, another important insulator in the semiconductor industry [9, 25, 26]. An experimental determination of the wavefunction character of the conduction band is not so simple here. The method *par excellence* to determine the wavefunction character of conduction bands experimentally is x-ray absorption spectroscopy (XAS). Excitations from a core level are very much confined to the atom (or ion), so the *local* density of states of the conduction band is probed. Unfortunately, it cannot be applied here since the dipole selection rules require an initial state of p symmetry to probe the s character of the conduction bands, and elements in the second period of the periodic table do not posses p electrons in the core. This motivates the present computational study also.

Alumina (α-Al_2O_3) with the corundum structure has a rhombohedral cell with $a = 5.136$ Å and $\alpha = 55.28°$, space group R-$3c$, no 167, which contains two formula units. There are four Al atoms at the Wyckoff positions c (0.352, 0.352, 0.352) and six O atoms at positions e (0.556, 0.944, 1/4) [27]. Each Al atom has three nearest-neighbour oxygen atoms at a distance of about 1.85 Å and three next-nearest oxygen atoms at a distance of about 1.98 Å. Aluminium nitride (AlN) with the wurtzite structure has a hexagonal cell with $a = 3.111$ Å and $c = 4.978$ Å, space group $P63mc$ no 186 [27]. There are two formula units in the cell. Both Al and N atoms occupy the 2b sites with Al at (1/3, 2/3, 0.0) and N at (1/3, 2/3, 0.385). Each atom in the structure is tetrahedrally coordinated, with Al–N distances of about 1.92 Å.

First-principles band-structure calculations were performed using the localized spherical wave (LSW) method [28], which gives a clear picture about the role of the orbitals. We used local-density exchange–correlation potentials [29] inside the space-filling and therefore overlapping spheres around the atomic constituents. Iterations were performed with k-points distributed uniformly in an irreducible part of the first Brillouin zone (BZ), corresponding to a volume of the BZ per k-point of about 1×10^{-7} Å^{-3}. As the crystal structures are not close-packed, empty spheres (atoms with zero nuclear charge) are put at interstitial sites. In the construction of the LSW basis [28, 30], spherical waves were augmented by solutions of the scalar-relativistic radial equations with angular momentum up to $l = 2$ for all the atoms, that is, we employed the basis set with the atomic-like symbols 2s/3s, 2p for O and N, 3s, 3p for Al, as well as 1s and 2p for empty spheres; 3d (Bessel) orbitals are included in the expansion of outgoing Hankel-functions in all neighbouring spheres. We performed calculations with the two basis sets: one without the O/N 3s and one with the O/N 3s states. The Wigner–Seitz sphere is 0.85 Å for Al, 1.37 Å for O and N, as well as 1.06 Å for empty spheres at 2c (1/2, 1/2, 1/2) in alumina, and 1.22 Å for empty spheres at (0, 0, 0.635) in AlN. The Wigner–Seitz radii for Al, O and N spheres correspond to the ionic radii [31].

The calculated band structures for α-Al_2O_3 and AlN are shown in figures 1 and 2, respectively. Some important characteristics of the band structures are summarized in table 1. As shown in figures 1 and 2, the different basis sets have a negligible influence on the valence bands for both α-Al_2O_3 and AlN. Both valence bands consist of two parts: the O/N 2s states dominate the lower part with a width of about 3 eV. That is not included in the figures but is summarized in table 1. The O 2s electrons are positioned about 4 eV in energy deeper than those of N 2s. The Fermi level is set arbitrarily at the top of the valence band. The width
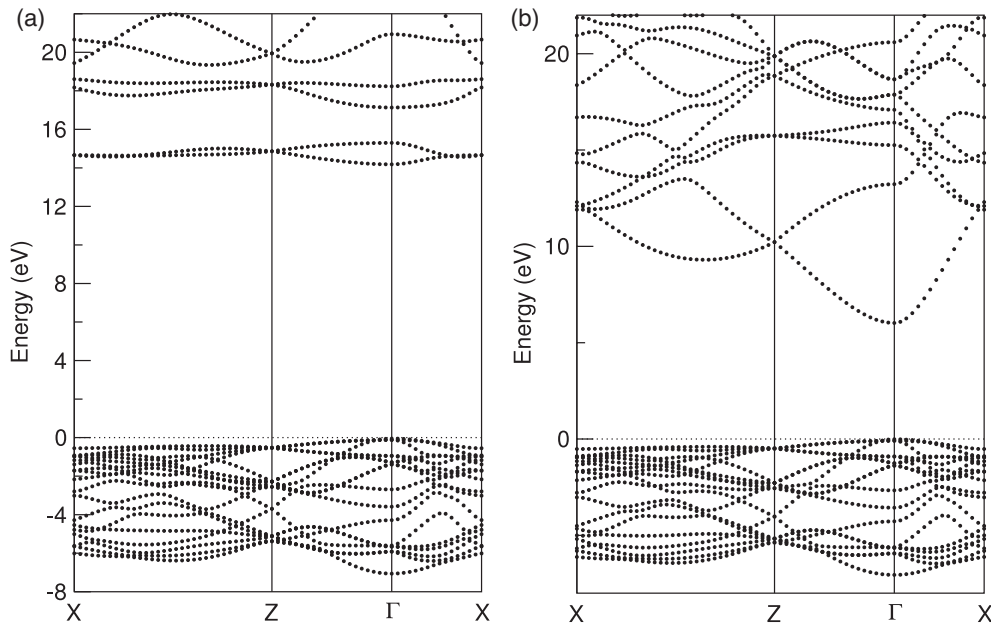
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Figure 1. Dispersion curves along the high symmetry lines in the BZ for alumina without O 3s states (a) and with O 3s states (b).

Table 1. Characteristics of the electronic structures of α-Al_2O_3 and AlN with different basis set. The experimental values are included for comparison.

	α-Al_2O_3			AlN		
	Band gap (eV)	Band width of O 2p (eV)	Band width of O 2s (eV)	Band gap (eV)	Band width of N 2p (eV)	Band width of N 2s (eV)
Without O/N 3s	14.10	7.10	3.14 (−19.34 to −16.20)	6.40	6.20	3.01 (−15.25 to −12.24)
With O/N 3s	5.98	7.10		4.40	6.20	
Exp. values	8.28 [8, 9]			6.26 [10]		

of upper part of the valence band is dominated by O/N 2p electrons. The O 2p electrons have a band width of about 7.1 eV, larger than that (6.4 eV) of N 2p, as shown in table 1. Those results agree well with the former theoretical calculations for α-Al_2O_3 [8, 11–13] and for AlN [32–34].

Before discussing band gaps it is important to realize that calculations based on the density-functional theory (DFT) underestimate band gaps typically by 30% for the systems considered here [35]. The origin of this discrepancy is in the neglect of the discontinuity of the exchange and correlation potential at the Fermi energy [36]. This implies that this 30% deviation should be taken into account in comparing calculated and measured band gaps. Thus a correct description of the conduction band results in DFT band gaps of 5.8 and 4.4 eV for the oxide and nitride, respectively. The influence of the O/N 3s orbitals on the electronic structure of the compounds is significant in the conduction bands, as shown in figures 1 and 2. Without oxygen 3s orbitals, the lower part of the conduction band for alumina is composed predominantly of Al 3s states. The calculated band structure without
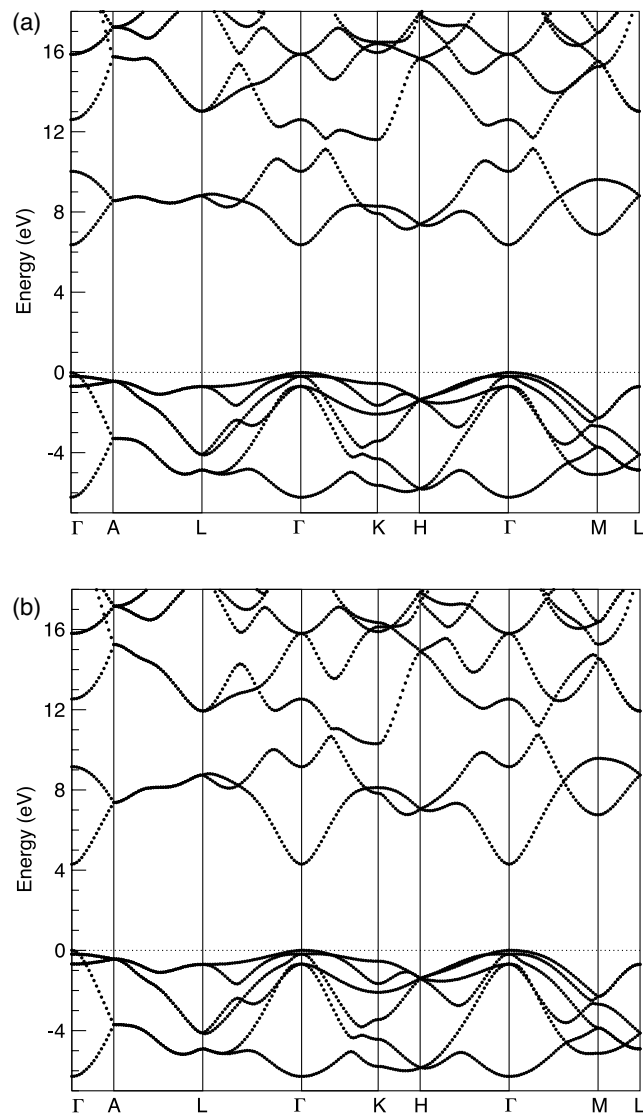
Figure 2. Dispersion curves along the high symmetry in the BZ for AlN without N 3s states (a) and with N 3s orbitals (b).

O 3s (figure 1(a)) gives the position of the conduction band too high, with an energy gap of about 14 eV, which is significantly *larger* than the experimental value (about 8.3 eV) [8, 9]. The band gap of the conduction band becomes significantly lower when the O 3s orbitals are used in the calculations. A band gap of about 6.0 eV was obtained (figure 1(b) and table 1). The calculated energy gap is about 30% lower than the experimental value, a typical local-density approximation (LDA) result [35]. The lower part of the conduction band is dominated by the characters of O 3s states, although some aluminium s character (about 15%) remain.

As shown in figure 2(a), the calculations without N 3s states give an energy gap of about 6.4 eV, which is very close to the experimental value (about 6.3 eV) [10]. The lower part of the conduction band is composed mainly of Al 3s states. However, such agreement is just

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superficial. The calculations with N 3s states in the basis set give a band gap of about 4.4 eV (figure 2(b)), which is about 30% smaller than the experimental value. Again that is a typical LDA result [35]. The calculations also showed that the lower part of the conduction band originates from both N 3s and to a lesser extend from Al orbitals.

The position of aluminium nitride and alumina is in between the regular III–V semiconductors on the one hand and main-group oxides and halides on the other hand. The size of the band gap is still dependent on the presence of anion 3s states, strong for alumina, less so for aluminium nitride. But the wavefunction character of the bottom of the conduction band does contain metal character, and also there is a clear influence of the size of the band gap on the metal (compare 4.7 eV for β-Ga_2O_3 and 3.4 eV for GaN) [37, 38]. The intrinsic charge carriers in alumina and aluminium nitride are holes of O/N 2p character or electrons of O/N 3s character with some admixture of metal states. These results are important in understanding the mechanisms for electron tunnelling and optical spectra of defects like F-centres, as well as many catalysis processes involving alumina and aluminium nitride.

Acknowledgments

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