

substance: titanium oxide (TiO₂)

property: band structure, band structure energies in rutile

band structure: Fig. 1 (tight binding calculation with next Ti – O, Ti – Ti, O – O neighbour interaction only and two empirical fitting parameters), Brillouin zone: Fig. 2. Alternate calculation [77P, 78M] using tight binding for valence bands, pseudopotential for conduction band gives broader bands than observed and conduction band minimum at Γ with a close minimum at X, but not M.

band structure energies

theoretical

$W(\pi^*)$	1.4 eV	π^* -bandwidth	77V
$W(\sigma^*)$	2.7 eV	σ^* -bandwidth	
$W(2p)$	5.5 eV	2p-bandwidth	
$E(\pi^*)$	– 5.6 eV	centre of π^* -band	
$E(\sigma^*)$	– 3.3 eV	centre of σ^* -band	

band edges: valence band: Γ_3^+ , conduction band: $M_{1,2}$ with R_1^+ only 0.12 eV higher

experimental:

		assignment		
E_{peak}	– 5.6 eV (4.7) eV	π	peak positions in XPE spectra;	77R
	– 22.4 eV (3.4) eV	σ	see Fig. 3 for low energy part;	
	– 37.5 eV (2.4) eV	O:2s	total spectrum: [72F];	
		Ti:3p	values in brackets: half-max. widths	

Ti L_{III} emission

$E(F)$	– 1.6 eV	$1t_{2g} \rightarrow 2p_{3/2}$	peaks in X-ray band spectra;	72F
$E(A)$	– 5.6 eV	$2e_g \rightarrow 2p_{3/2}$	Fig. 4 shows the construction	
$E(G)$	– 7.9 eV	$2a_{1g} \rightarrow 2p_{3/2}$	of an empirical band scheme	
$E(X)$...	extended tailing	on which the assignment is made.	
$E(C)$	– 20.4 eV	$1e_g \rightarrow 2p_{3/2}$	Data of Ti K, O K, Ti L _{III} X-ray	
$E(D)$	– 22.9 eV	$1a_{1g} \rightarrow 2p_{3/2}$	band spectra, optical DOS,	
			absorption and photoconductivity	

Ti L_{III} absorption:

			have been used. Component X	
$E(f)$	– 2 eV	exciton (?)	artificially introduced to match	
$E(b)$	+ 1.5 eV	$2p_{3/2} \rightarrow 2t_{2g}$	lang-wavelength tail. Components	
$E(c)$	+ 3.6 eV	$2p_{3/2} \rightarrow 3e_g$	B, b, c primarily due to Ti; F, A,	

Ti K emission:

$E(K\beta_5)$	– 4.4 eV	$3t_{1u} \rightarrow 1s$	G, C, D primarily due to O.	
	– 6.1 eV	$2t_{1u} \rightarrow 1s$	All energies relative to E_F .	
$E(K\beta'')$	– 20.6 eV	$1t_{1u} \rightarrow 1s$		

Ti K absorption

$E(b)$	+1.5 eV	$1s \rightarrow 2t_{2g}$
$E(c)$	+3.6 eV	$1s \rightarrow 3e_g$
$E(d)$	+9.9 eV	$1s \rightarrow 3a_{1g}$
$E(e)$	+17.3 eV	$1s \rightarrow 4t_{1u}$

O K emission

$E(B)$	− 3.1 eV	$t_{2u}, t_{1g} \rightarrow 1s$
$E(A)$	− 5.3 eV	$2e_g \rightarrow 1s$
$E(C)$	− 6.4 eV	$2t_{1u} \rightarrow 1s$

O K absorption

$E(f)$	− 1 eV	exciton (?)
$E(b)$	+1.5 eV	$1s \rightarrow 2t_{2g}$
$E(c)$	+3.6 eV	$1s \rightarrow 3e_g$
$W(2p)$	6.3 eV	
$E(\sigma)-E(\pi)$	4.0 eV	
$W(2s)$	2.5 eV	
$E(\sigma)-E(2s)$	14.5 eV	
$E(\sigma^*)-E(\pi^*)$	2.1 eV	

bandwidths and differences in
mean band energies deduced
from data above

References:

- 72F Fischer, D. W.: Phys. Rev. B5 (1972) 4219.
- 77P Pascual, J., Camassel, J., Mathieu, H.: Phys. Rev. Lett. 39 (1977) 1490.
- 77R Riga, J., Teuret-Noel, C., Pireaux, J. J., Caudano, P., Verbist, J. J., Gobillon, Y.: Physica Scr. 16 (1977) 351.
- 77V Vos, K.: J. Phys. C10 (1977) 3917.
- 78M Mathieu, H., Pascual, J., Camassel, J.: Phys. Rev. B18 (1978) 6920.

Fig. 1.

TiO₂, rutile. Band structure. Left: Energy vs. wave vector along symmetry lines in the Brillouin zone, right: schematic bands with nomenclature used in the tables [77V].

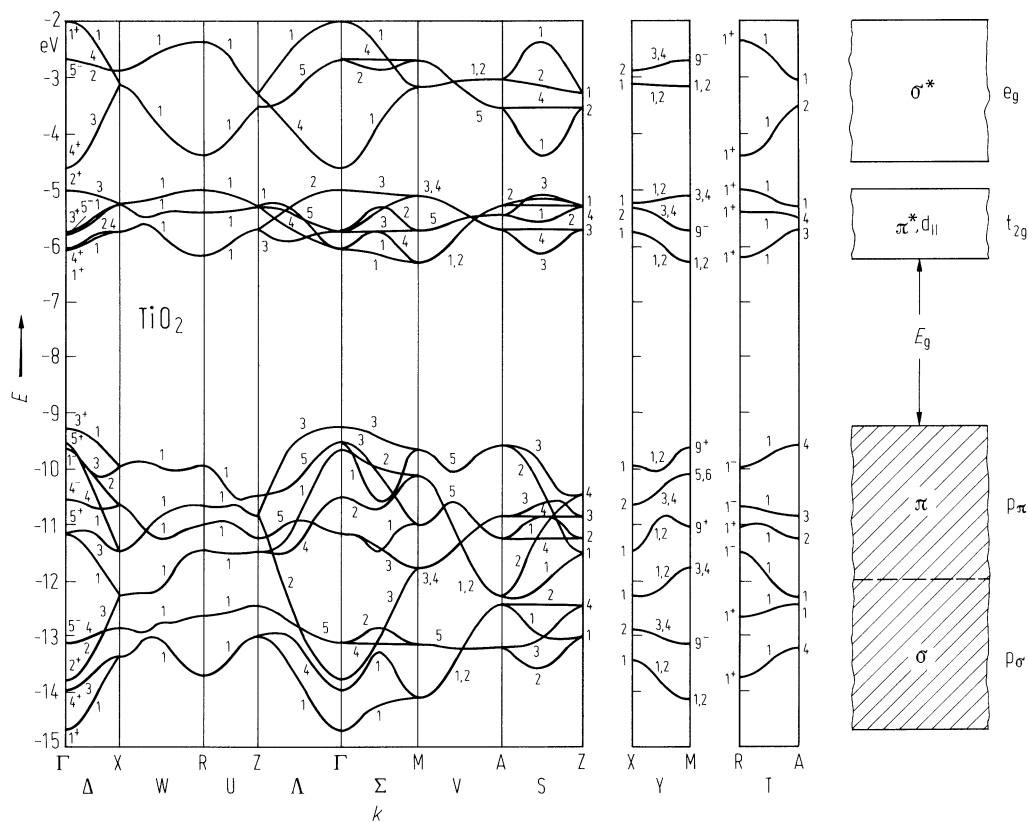


Fig. 2.

TiO₂, rutile. (a) Unit cell, (b) Brillouin zone [77V]. Distances in Å.

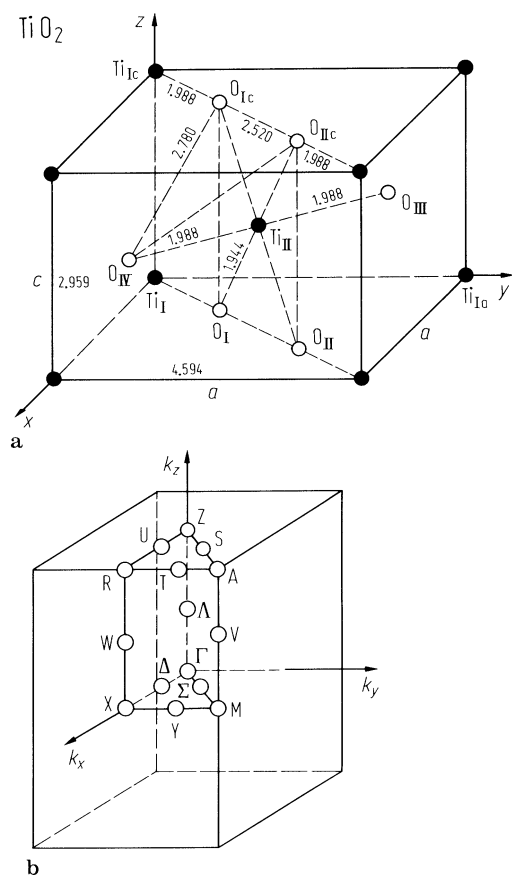


Fig. 3.

TiO_2 . XPE spectrum (intensity vs. electron binding energy $E_b = E - E_F$). For comparison the spectra for RuO_2 and IrO_2 are also shown [77R]. The dashed line for IrO_2 refers to the second derivative of the XPE spectrum.

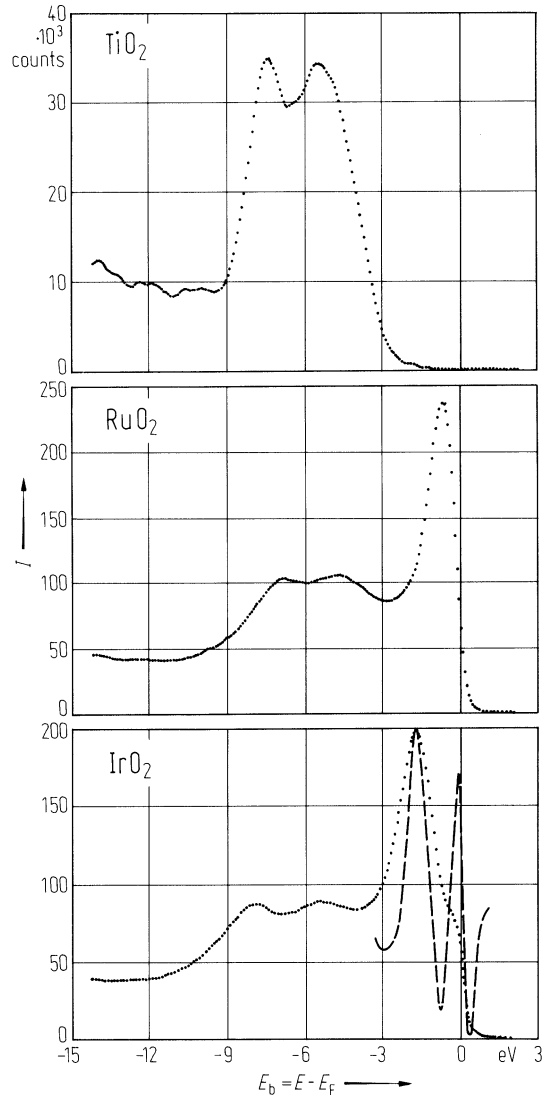


Fig. 4.

TiO₂. Empirical energy level scheme (relative intensity of analyzed spectra vs. electron binding energy). For comments to the insets and the designations, compare the tables [72F].

