

substance: titanium oxide (TiO₂)

property: energy gap, further interband transitions in rutile

energy gaps

There is considerable controversy over the assignment of the fundamental optical absorption edge in rutile. Assignments based on two different band-structure calculations [77V, 77D] have been reported, and the most important difference is that [78P] conclude, on the basis of [77D], that the edge is indirect for $E \parallel c$ but there is a lower-energy, direct forbidden edge for $E \perp c$, whereas [77V] concludes that the edge is indirect on both polarizations.

$E_{g,dir}$	3.033 eV	$T = 1.6 \text{ K}; E \perp c$	direct forbidden edge preceded by a 1s exciton at 3.031 eV (the transition is indirect for $E \parallel c$)	78P
	3.038 eV	$T = 80 \text{ K}$		
	3.062 eV	$T = 298 \text{ K}$		
$E_{g,ind}$	3.049 eV	$T = 1.6 \text{ K}; E \parallel c, E \perp c$	indirect edge; edges at 3.060 and 3.064 eV due to emission of TA and O ₁ phonons, respectively. Identical edges found for $E \perp c$ see Fig.2.	78P
	3.057 eV	$T = 80 \text{ K}; E \parallel c, E \perp c$	Transition edges at 3.042 and 3.046 eV due to absorption of O ₁ and TA phonons and at 3.068 eV due to TA phonon emission	
	3.101 eV	$T = 298 \text{ K}; E \parallel c, E \perp c$		

Support for the above assignment comes from optical measurements on stressed crystals; they suggest that the two phonons, O₁ at 15meV and TA at 11 meV, are associated with the point 0.3 ($2\pi/a$) [100] in the Δ direction, and the direct transition with $\Gamma_{3v} \rightarrow \Gamma_{1c}$ [78M].

Rather different conclusions have been drawn from the electroreflectance data of [77V].

$E_{g,ind} (\Gamma_{3v}^+ \rightarrow M_{1,2c})$	3.005 eV	$T = 80 \text{ K}; E \perp c$	edge associated with a M_9^+ phonon at 3.037 eV	77V
$(\Gamma_{5v}^+ \rightarrow M_{1,2c})$	3.013 eV	$T = 80 \text{ K}; E \parallel c$	edge associated with a M_9^- phonon at 3.069 eV	

further interband transitions

$E(\Gamma_{3v}^+ \rightarrow R_{1c}^+)$	3.06...3.11 eV	$T = 80 \text{ K}; E \perp c, E \parallel c$	associated with R_1^- ; phonon at 3.124 eV	77V
$E_{g,dir}(\Gamma_{5v}^+ \rightarrow \Gamma_{1,4c}^+)$	3.57 eV	$T = 80 \text{ K}; E \perp c$	Pronounced structure above this edge in Fig. 1 due to transitions between energy-band regions near the Σ symmetry line of BZ. Further direct transitions due to $\Gamma_{1v}^- \rightarrow \Gamma_{1c}^+$ and $\Gamma_{5v}^+ \rightarrow \Gamma_{5c}^-$ are found above 3.6 eV in $E \parallel c$	

fundamental edge dichroism

(ascribed to $\Gamma_{3v}^+ - M_{1,2c}$ transitions for $E \perp c$ and $\Gamma_{5v}^+ - M_{1,2c}$ transitions for $E \parallel c$)

$D(E_{g,ind}(E \parallel c))$	11.5 meV	$T = 298$ K	61S
$D(E_{g,ind}(E \perp c))$	12 meV	$T = 77$ K	75A
	15 meV	$T = 77$ K	66A
	33 meV	$T = 77$ K	74V
	33 meV	$T = 4.2$ K	75A

temperature and pressure dependence of energy gaps

$dE_{g,ind}/dp$	$1.19 \cdot 10^{-6}$ eV bar ⁻¹	RT	wavelength-modulated absorption	77P, 78M
$dE_{g,ind}/dT$	$1.98 \cdot 10^{-4}$ eV K ⁻¹	$T > 60$ K		78P
$dE_{g,dir}/dp$	$1.17 \cdot 10^{-6}$ eV bar ⁻¹	RT		78M
$dE_{g,dir}/dT$	$1.77 \cdot 10^{-4}$ eV K ⁻¹	$T > 60$ K		78P
$(E_{g,ind})_T = (E_{g,ind})_0 + 2.363 \cdot 10^{-4} T^2 / (T + (\Theta_D/10))$ [eV]	Θ_D : Debye temperature taken as 758 K, $(E_{g,ind})_0 = 3.0489$ eV,			80G
$(E_{g,dir})_T = (E_{g,dir})_0 + 1.245 \cdot 10^{-4} T^2 / (T + (\Theta_D/10))$ [eV]	$(E_{g,dir})_0 = 3.0329$ eV			

References:

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Fig. 1.

TiO₂. (a) Real and imaginary parts of the dielectric constant. Left: $E \perp c$, right: $E \parallel c$; dotted curves $T = 300$ K, solid curves $T = 80$ K; (b) $\Delta\epsilon_1$ and $\Delta\epsilon_2$ as calculated from the electroreflectance spectrum at 300 K. Heavily drawn curves correspond to electrolyte configuration and lightly drawn curves to dry configuration. Broken curves $\Delta\epsilon_1$, full curves $\Delta\epsilon_2$. Numbers refer to estimated gold thickness in Å (measurements with gold electrodes evaporated onto crystal surface) [77V].

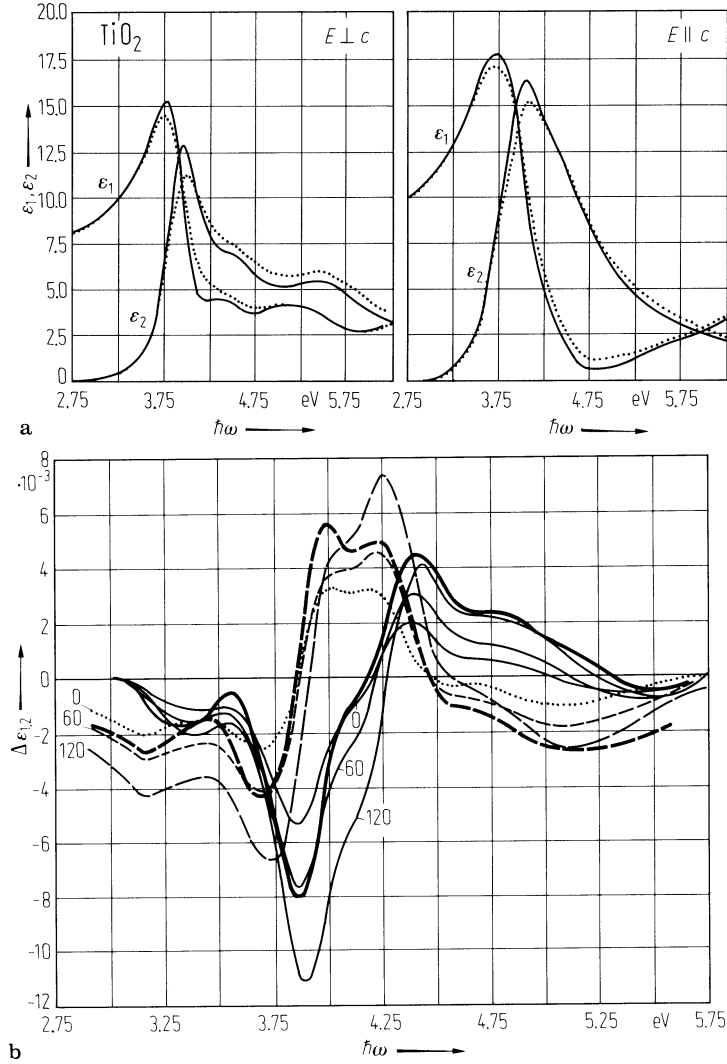


Fig. 2.

TiO₂. (a), (b) Square root of the absorption coefficient vs. photon energy near the absorption edge for $E \parallel c$ (a) and $E \perp c$ (b), inset in (b) shows 1s exciton; (c) wavelength modulated spectrum (differential of ΔK vs. photon energy) at 1.6 K [78P]. e-TA, a-O₁: emission of TA phonons, absorption of O₁ phonons.

