

**substance: titanium oxide (TiO<sub>2</sub>)**

**property: ESR parameters of native defects in pure n-type TiO<sub>2-x</sub> (rutile)**

	$e_{CB^-}$	$S$	principal axes	$g$ -value	$e_{CB^-}$ : number of conduction band electrons per defect $S$ : spin quantum number
V <sub>O</sub> <sup>••</sup>	2	0			
Ti <sub>i</sub> <sup>3•</sup>	3	1/2	[001]	1.941 ( $g_{\parallel}$ ) 1.976(2) ( $g_{\perp}$ )	At lowest x, ESR signal is broader and has principal axes in basal plane [100] + 26°, [010]+26° with $g = 1.974$ and $1.977$ and $1.941$ respectively. At higher x, a new ESR signal C is seen which may be of the same origin as A [72H1] but motionally narrowed by electron hopping from centre to centre. Superhyperfine field shows electron spread over near-neighbour Ti. [73O, 74S] have identified low temperature A-signal as due to interstitial protons, but C-centre has been reaffirmed [77Y2] as derived from isolated Ti <sup>3+</sup> <sub>i</sub> .
Ti <sub>i</sub> <sup>4•</sup>	4	0			
(Ti <sub>i</sub> <sup>3•</sup> ) <sub>2</sub>	6	1	[001] [110] [110]	1.951(2) 1.9803(5) 1.9747(5)	X-centre
(Ti <sup>3+</sup> -Ti <sup>3+</sup> ) APB	0	0			trapped e <sup>-</sup> spin-paired
(Ti <sup>3+</sup> -Ti <sup>4+</sup> ) APB	1	1/2	[001] [100]+4.5° [010]+4.5°	1.791(3) 2.053 1.835	W-centre. Whether (Ti-Ti) APB traps one or two electrons depends on Ti-Ti separation; only one trapped electron gives ESR signal as two trapped electrons are spin-paired in Ti - Ti bond.
(Ti <sup>4+</sup> -Ti <sup>4+</sup> )APB	2	0			
(Ti <sup>3+</sup> -Ti <sup>3+</sup> ) <sub>bulk</sub>	2	0			
(Ti <sup>4+</sup> -Ti <sup>4+</sup> )CS	2	0			

Fig. 1 shows the variation of ESR signal intensity with oxygen deficit. The low-temperature A-signal is not intrinsic [74S] but associated with interstitial hydrogen, and the so-called vacuum reduction of  $\text{TiO}_2$  can only be effected in vacuum system with residual impurities;  $\text{TiO}_2$  cannot be reduced by heating in a clean vacuum [73O]. The weight of ESR evidence is nevertheless in favour of interstitial Ti rather than  $\text{V}_0^{\cdot\cdot}$  at moderate ( $x \approx 10^{-4}$ ) deviations from stoichiometry and possible interstitial sites are shown in Fig. 2. Other evidence for interstitials derives from proton channeling experiments [77Y1] on "vacuum reduced"  $\text{TiO}_2$ .

Ordered defects exist on shear planes [69B, 77Y2]. At low defect concentrations the main defect line is along [312] (Fig. 3) and isolated planar {312} defects have been found for  $x \geq 0.001$ . The (312) CS planes show a net attraction (Fig. 4) and at higher deviation from stoichiometry they order to produce higher members of the homologous series  $\text{Ti}_n\text{O}_{2n-1}$  ( $15 \leq n \leq 37$ ) [69B, 71B1, 71B2]. As  $n$  decreases the shear planes are observed to swing around to (121) via a very large number of intermediate orientations (hkl) that can be resolved into  $(hkl) = p(121) + q(011) = (p, 2p+q, p+q)$  ( $p, q$  integers). This "swinging process" has little effect on the CS separation, and its onset appears to be at  $x \approx 0.05$  though work on  $(\text{Ti,Cr})\text{O}_{2-x}$  suggests that CS swinging commences at much smaller values of  $x$  ( $\approx 0.02$ ) in this system.

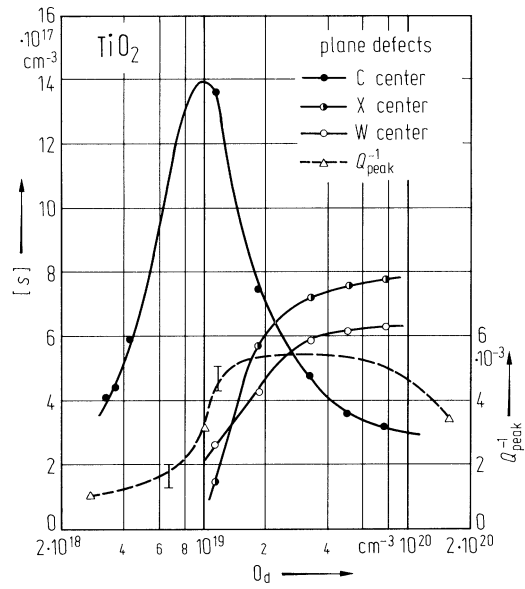
The type of defect formed as well as the level of ordering depends critically on the purity and previous history of the sample, and reproducible results are only obtained for samples annealed under controlled conditions for lengthy periods. The ubiquity of interstitial hydrogen revealed by EPR may also be of considerable significance. Apparently reduction by  $\text{CO}/\text{CO}_2$  mixtures rather than by "vacuum" can arrest the formation of shear planes [80B] though this surprising result lacks confirmation.

## References:

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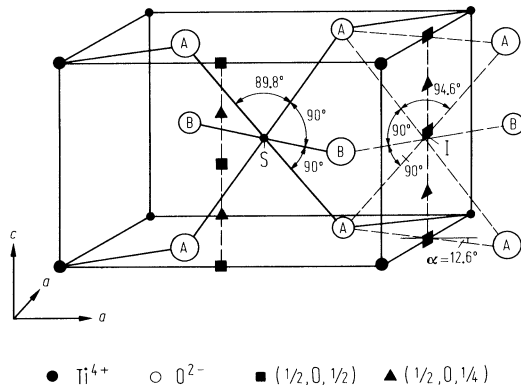
**Fig. 1.**

TiO<sub>2</sub>. Concentration of various lattice defects in slightly reduced rutile vs. oxygen deficit O<sub>d</sub> (left ordinate spin concentration, right ordinate internal friction peak) [72H1].



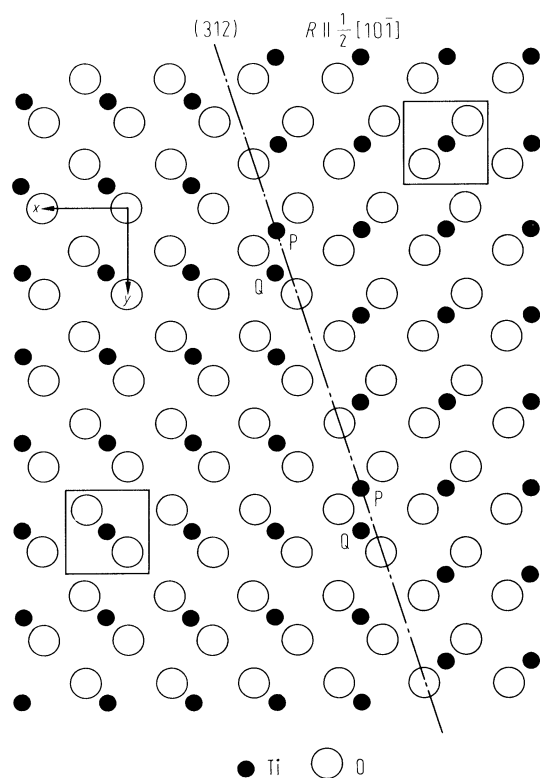
**Fig. 2.**

TiO<sub>2</sub>. Crystal structure of rutile showing some  $[1/2,0,1/2]$  and  $[1/2,0,1/4]$  types of interstitial site. Substitutional (S) and interstitial (I) site distances to oxygen atoms are: AS = 1.944 Å, BS = 1.988 Å, AI = 2.184 Å, BI = 1.603 Å ( $a = 4.594$  Å,  $c = 2.959$  Å) [73K].



**Fig. 3.**

TiO<sub>2</sub>. Projection of rutile lattice onto the (001) plane intersected by a (312) fault. Ti-ion pairs PQ about the fault, and a single electron trapped at this site produces a W-centre EPR spectrum [77Y2]. *R*: Ti-Ti displacement.



**Fig. 4.**

TiO<sub>2</sub>. Schematic empirical interaction energy between a pair of (312) CS-planes: wave function  $\Psi(i,j)$  vs. plane separation  $D_0$  [72B].

