substance: titanium oxide (TiO_2)
property: defects in non-stoichiometric TiO_{2-x} (rutile)

nature of defects - direct evidence: The most important distinction is between ordered shear planes [72B] and point defects [72K]. Estimates [72H, 76B, 77B] put x as $\approx 2\cdot10^{-4}$ and $8\cdot10^{-3}$ as the upper limit of the point defect region. In this region the main argument has lain between which process of the two shown is dominant

(I) $TiO_2 \rightarrow TiO_{2(l-x)} + xO_2 + 2xV_0^{\cdot\cdot} + 4xe^-$
(II) $TiO_2 \rightarrow (1-x)TiO_2 + xO_2 + xTi_i^{3\cdot} + 3xe^-$, $xTi_i^{3\cdot} \rightarrow xTi_i^{4\cdot} + xe^-$. (For $V_0^{\cdot\cdot}$, Ti_i; etc., see document **native defects in pure n-type TiO_{2-x} (rutile)**)

Although theoretical calculations [77J] suggest that (I) should dominate, the experimental situation is confused. No ESR study on single-crystal TiO_{2-x} has identified $V_0^{\cdot\cdot}$, though indirect methods have strongly implied that $V_0^{\cdot\cdot}$ may dominate for very small x [72K, 67A]. Larger values of x and higher reduction temperatures have been suggested as favouring (II) [67K, 69B], but oxygen diffusion experiments [72I] have been interpreted as implying that oxygen vacancies also form even at considerable deviations from stoichiometry.

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