substance: titanium oxide (TiO_2)
property: transport properties in non-stoichiometric TiO_{2-x}: conductivity and defect distribution

Results of calculations using the model discussed in document are compared with experimental conductivity data in Fig. 1. Additional data: Fig. 2. In the compositional range $1 \cdot 10^{19}$ cm^{-3} < O_d < $5 \cdot 10^{19}$ cm^{-3} (O_d: oxygen deficiency), the equilibrium low-temperature defect concentration decreases with increasing O_d as $Ti_i^{3\cdot}$ centres first form pairs $(Ti_i^{3\cdot})_2$ and then clusters of pairs at an APB prior to establishment of (hkl) CS planes [72H]. Formation of (hkl) CS aggregates increases with *O*d (D_{sp} within aggregate corresponds to n ≈ 35 to 40 of a Ti_nO_{2n-1} phase) prior to condensation into a definite phase of the homologous series. From table above, *n* increases sharply with O_d in range of point defects and $(Ti_i^{3\cdot})_2$ pairs, but decreases with increasing O_d in compositional range where point defects are suppressed by formation of planar defects. Fig. 5 shows evolution of defect populations as observed by direct methods. The associated decrease in *n* with increasing O_d in the range $1 \cdot 10^{19}$ cm^{-3} < O_d < $5 \cdot 10^{19}$ cm^{-3} is manifest in the low temperature conductivity (Figs. 3, 4) as a minimum in ρ vs. O_d. Note that this behaviour is to be distinguished from the impurity-band formation with increasing impurity concentration found in conventional broad-band semiconductors.

References:

66B1 Blumenthal, R. N., Coburn, J., Baukus, J., Hirthe, W. M.: J. Phys. Chem. Solids 27 (1966) 643.
66B2 Blumenthal, R. N., Kirk, J. C., Hirthe, W. M.: J. Phys. Chem. Solids 28 (1966) 1077.
67K Kofstad, P.: J. Less-Common Met. 13 (1967) 635.
70H Hasiguti, R. R., Yagi, E., Aono, M.: Radiat. Eff. 3-4 (1970) 137.
72H Hasiguti, R.: Adv. Mater. Sci. 2 (1972) 69.

Fig. 1.

TiO_{2-x}. Defect concentration vs. oxygen pressure from Kofstad model [67K] and comparison with conductivity data of [66B1] for 1500ºC (left hand figure) and 1100ºC (right hand figure). *n*: concentration of defects, σ along [0 0 1] direction. 1 atm = 101325 Pa.

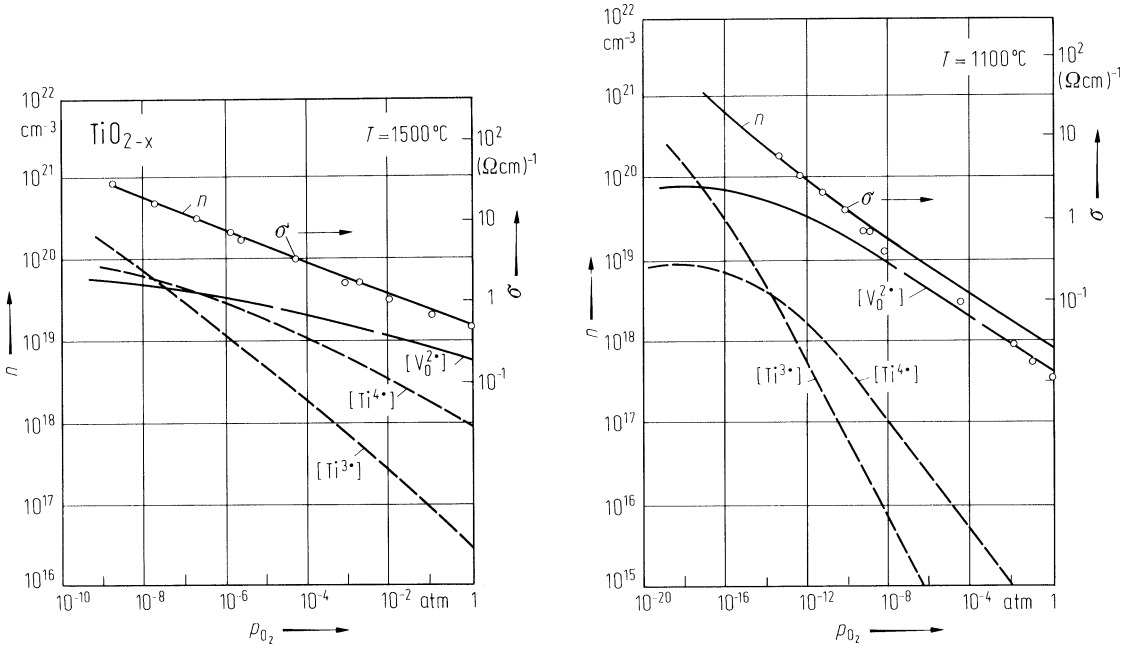

Fig. 2.

TiO_{2-x}. Conductivity vs. oxygen partial pressure for various temperatures; current in [001] direction, single crystals [66B1, 66B2].

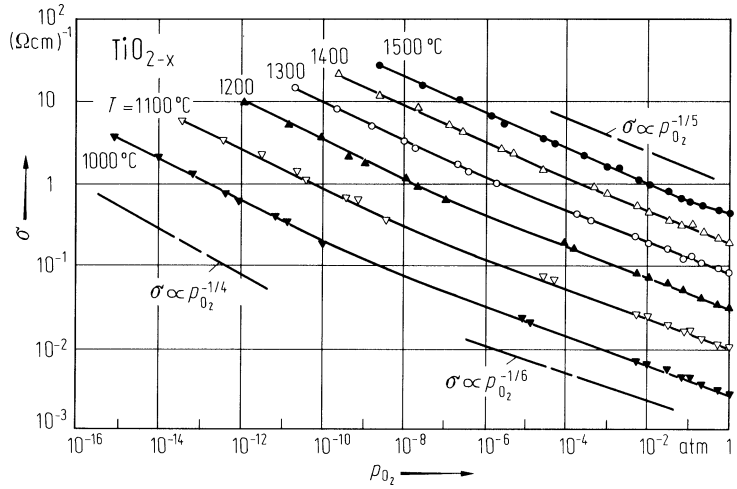

Fig. 3.

TiO_{2-x}. Resistivity and Hall coefficient vs. reciprocal temperature for slightly reduced TiO_2. Oxygen deficit range: $3.7 \cdot 10^{18}$ to $13 \cdot 10^{18}$ cm^{-3} [72H, 70H]. (Orientation not specified.)

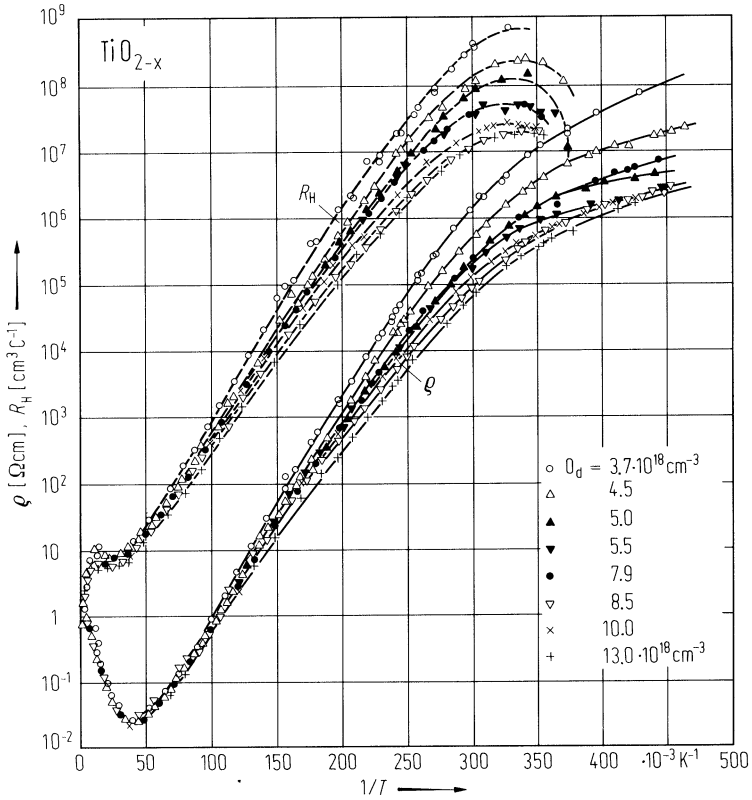

Fig. 4.

TiO_{2-x}. Resistivities at 4 K and 300 K vs. oxygen deficiency of slightly reduced material [72H, 70H]. (Orientation not specified.)

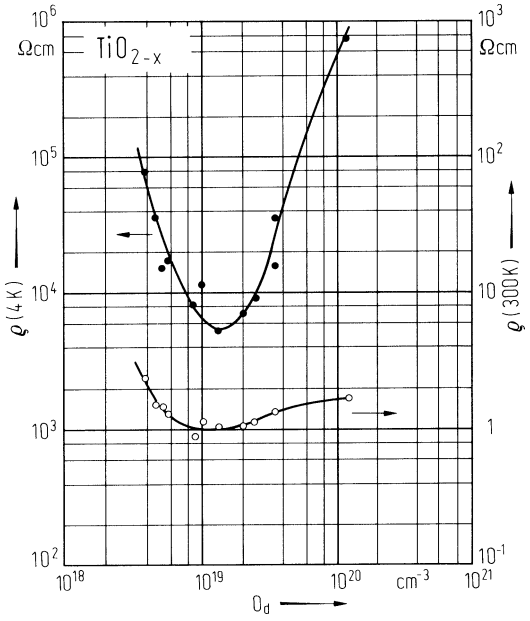

Fig. 5.

TiO_{2-x}. Concentration of various lattice defects in slightly reduced rutile vs. oxygen deficit O_d (left ordinate spin concentration, right ordinate internal friction peak) [72H].