substance: titanium oxide (TiO_2)
property: transport properties in non-stoichiometric TiO_{2-x}: resistivity vs. T^{-1}

Above 300 K (Fig. 1) samples with oxygen deficiencies in the critical range $1.8 \cdot 10^{19}$ $cm^{-3} < O_d < 2 \cdot 10^{20}$ cm^{-3} exhibit three distinct temperature regions: Region "a" having an independent $E_A{}^a$ = 0.028 eV, region "b" having an O_d-dependent $E_A{}^b = E_0 + \beta O_d{}^{1/3}$ with $E_0 \approx 0.0080$ eV and $\beta \approx 8.8 \cdot 10^{-9}$ eV cm, and an exhaustion region "c" [74I]. Typical data for such samples, obtained by measurements in the [110] direction, are given in the following table (cf. Fig. 1) [74I]:

Specimen	1	2	3	4	5	6
Reduction (temperature [K] · time [h])	1073 · 368	1073 · 368 + 1173 · 164	1173 · 160	1173 · 160 + 1273 · 45	1073 · 368 + 1173 · 164 + 1273 · 230	1173 · 160 + 1273 · 45 + 1373 · 40
Exhaustion temperature [K]	≈ 900	≈ 1000	≈ 1000	≈ 1100	≈ 1100	≈ 1200
ρ [Ω cm] in exhaustion range	2.76	1.60	1.06	0.91	0.71	0.50
μ [cm^2/V s] in exhaustion range	$6.42 \cdot 10^{-2}$	$4.93 \cdot 10^{-2}$	$4.93 \cdot 10^{-2}$	$3.89 \cdot 10^{-2}$	$3.89 \cdot 10^{-2}$	$3.12 \cdot 10^{-2}$
Concentration of electrons, n [cm^{-3}]	$3.5 \cdot 10^{19}$	$7.9 \cdot 10^{19}$	$1.2 \cdot 10^{20}$	$1.8 \cdot 10^{20}$	$2.3 \cdot 10^{20}$	$4.00 \cdot 10^{20}$
Concentration of deficient oxygens, O_d [cm^{-3}]	$1.8 \cdot 10^{19}$	$4.0 \cdot 10^{19}$	$6.0 \cdot 10^{19}$	$8.8 \cdot 10^{19}$	$1.1 \cdot 10^{20}$	$2.00 \cdot 10^{20}$

The peculiar increase in E_A with increasing O_d appears to reflect a clustering of donor centres, i.e. the condensation of $(Ti_i{}^{3\cdot})_2$ into $(Ti^{3+} - Ti^{3+})$ APB's of increasing area. Hall measurements on single crystal samples cut perpendicular to the *c*-axis also showed a change from simple to complex behaviour with increasing O_d suggestive of defect clustering at the higher concentrations [64A].

At high oxygen partial pressures, it is necessary to take into account the influence of impurities (see second next document).

It seems reasonably well established [76B, 77B1, 77B2], that at elevated temperatures, the onset of diphasic behaviour occurs at a somewhat larger value of x than suggested by low-temperature EPR and electron microscopy data. Thus the apparent success of point defect models for TiO_2 at $T > 1300$ K [67K] for values of x as high as 0.01 can be understood on this basis.

References:

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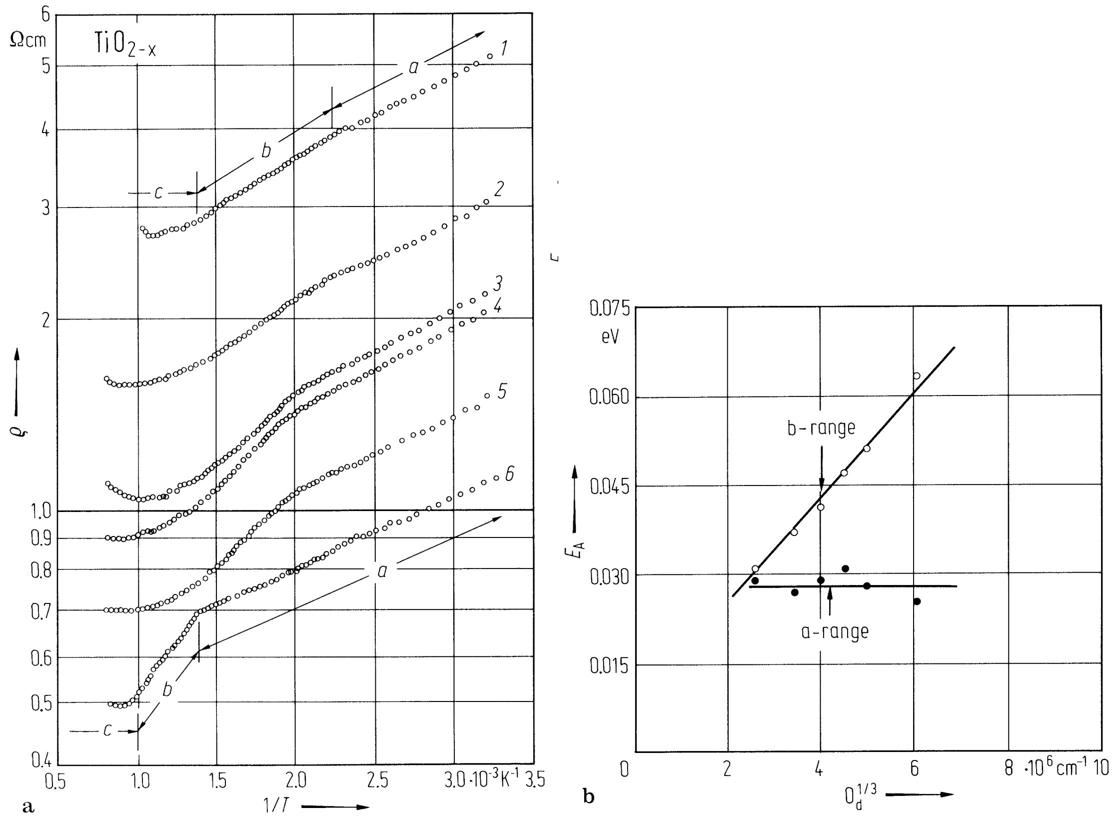
Fig. 1.

TiO_2. (a) Resistivity in the [110] direction of moderatly reduced TiO_2 vs. reciprocal temperature, (b) dependence of activation energy in ranges a and b on oxygen deficiency. For data on the samples 1...6, see the tables [59G, 74I].



a **b**