

substance: titanium oxide (TiO₂)

property: transport properties in non-stoichiometric TiO_{2-x}: electron mobility

Measurements of the drift mobility are plagued by uncertainties in the estimate of n . For $O_d < 1 \cdot 10^{19} \text{ cm}^{-3}$, comparison of point-defect theory for n [72K] with measured (nearly isotropic) conductivity gives $\mu_{dr} \approx 0.2 \text{ cm}^2/\text{V s}$ at elevated temperatures ($T \approx 1200^\circ\text{C}$).

The IR reflectivity data could be fitted to a model in which the phonon modes for free carriers in n-type TiO₂ are coupled to LO phonon modes [77B1]. The mobility was found unactivated, and "dressed" effective masses of $8 \dots 10 m_0$ were obtained.

Thermal conductivity and thermoelectric power of single crystals show maxima at 15 K (see Fig. 1). Whereas κ is anisotropic ($\kappa_c/\kappa_a = 1.5(1)$) for $T > 25 \text{ K}$, S is not within 10.5% (Fig. 1) [65T]. Sample 2 in Fig. 1 had a thermal gradient along the c -axis, sample 1 along the a -axis. The steep increase in S with decreasing $T < 50 \text{ K}$ is attributed to phonon drag [55H].

From Seebeck data at 1260 K a mobility $\mu_a = 0.17 \text{ cm}^2/\text{V s}$ was obtained by [75O], in agreement with [72K]. Similar point defect model analysis by [81M] gives average μ -values of $0.06 \text{ cm}^2/\text{V s}$ at 1100°C up to $\approx 0.1 \text{ cm}^2/\text{V s}$ at 800°C . Extrapolation to RT gives $\mu \approx 0.3 \text{ cm}^2/\text{V s}$ [81M].

At low p_{O_2} , S varies as $p_{O_2}^{-1/5}$ in agreement with a point defect model involving interstitial Ti. At higher p_{O_2} , S rises rapidly and may even change sign (Fig. 2) implying a p-type conducting regime.

In contrast to [65T] a slight anisotropy in S ($5 \dots 7 \%$) is reported by [67B1, 67B2, 75B] which is very enhanced at higher donor concentrations. RT mobilities deduced from Seebeck data are $\mu_a = 0.16 \text{ cm}^2/\text{V s}$ and $\mu_c = 0.56 \text{ cm}^2/\text{V s}$. μ_a becomes activated above 300 K, μ_c above 500 K. Very high effective masses were reported ($100 \dots 150 m_0$) [68B] leading to the suggestion of small polaron behaviour [69A].

The Hall coefficients for fields parallel or perpendicular to the c -axis are different. With the assumption of a single conduction band, the effective mass can be calculated from R_H and $S = -(k/e)(A_n + (E_F/kT))$, where A_n depends on the scattering mechanism. For a RT resistivity of $1 \dots 10 \ \Omega \text{ cm}$: $m_n = 30 \dots 35 m_0$ at 300 K with $A_n = 20$, $m_n = 20 m_0$ with $A_n = 2.5$.

In the temperature interval $100 \text{ K} \leq T \leq 300 \text{ K}$ the mobile electrons can be considered to have a lower effective mass ($m_n = 3 \dots 5 m_0$) [64A] provided electron-phonon coupling gives a large-polaron mobility [62F]. The temperature dependence of μ_H is given in Fig. 3 below room temperature; Fig. 4 shows some representative results for temperatures above RT.

Fig. 5 shows dispersion of conductivity and dielectric constant at 300 K for a vacuum-reduced sample ($O_d \approx 1.8 \cdot 10^{17} \text{ cm}^{-3}$). The magnitude of the dispersion of conductivity is essentially temperature-independent below 300 K, which is compatible with strong electron-coupling to optical-mode phonons [68G].

The assumption of a single conduction band may need refinement. At the centre of the Brillouin zone, the Ti 3d orbitals of t_{2g} parentage are split by the tetragonal symmetry of the octahedral interstice; distinguishing the two orbitals π -bonding with the oxygen nearest neighbours from the orbital that σ -bonds with like nearest-neighbour cation orbitals along the c -axis gives the nomenclature π^* and $d_{||}$ in Fig. 7 for bands of t_{2g} parentage. Interpretation of the Hall coefficient anisotropy (Fig. 6) has been made on a model consisting of two conduction bands having their bottoms separated by about 0.05(1) eV [65B]. The Hall mobilities $\mu_{H||c}$ ($R_H(||a)/\rho||c$) and $\mu_{H\perp c}$ ($R_H(||c)/\rho||a$) are essentially independent of carrier concentration over a range of 10^6 , indicating they represent intrinsic properties. At 300 K, the Hall mobilities fall in the ranges $0.77 \leq \mu_{H||c} \leq 1.25$ cm²/V s and $0.15 \leq \mu_{H\perp c} \leq 0.35$ m [65B]. This model has been refined [66A] to a single ellipsoidal multivalley conduction band with longitudinal masses of ca. $50 m_0$ and transverse mass of ca. m_0 . If an isotropic model is used, the same data [66A] gives an average mass of 5...13 m_0 at 300 K. Alternatively, anisotropy in the phonon modes, apparent in the anisotropic thermal conductivity, may introduce anisotropy into a polaron mobility. This possibility has not been explored.

References:

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Fig. 1.

TiO_2 . Seebeck coefficient vs. temperature of reduced or Nb-doped rutile. Upper curve 0.1% Nb-doped. Curves 1, 2 heated at 1175°C at 10^{-5} mm Hg for 27 h, curve 3 hydrogen reduced sample [65T]. Curve 1: $S \parallel a$, curve 2: $S \parallel c$, curve 3: $S \parallel a$.

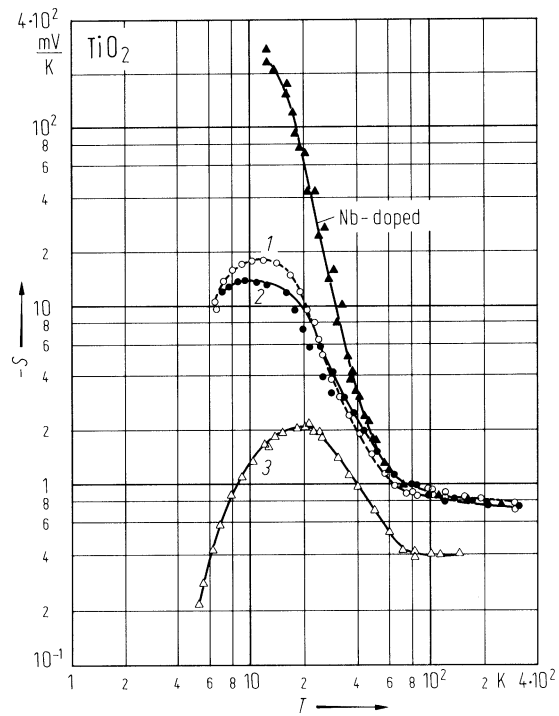


Fig. 2.

TiO_2 . Seebeck coefficient vs. oxygen partial pressure for polycrystalline rutile containing small quantities of Al and Fe. Temperature: circles 1573 K, full triangles 1471 K, open triangles 1393 K, full circles 1273 K. Lines are curves fitted to a suitable point-defect model [77B2].

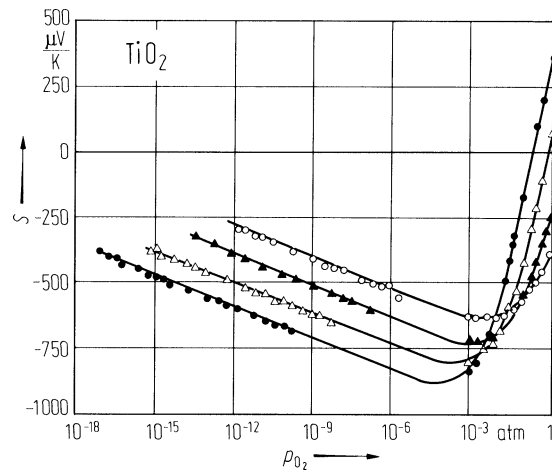


Fig. 3.

TiO₂. Hall mobility in [001] direction vs. reciprocal temperature below 300K [64A]. Different symbols refer to samples of differing resistivities.

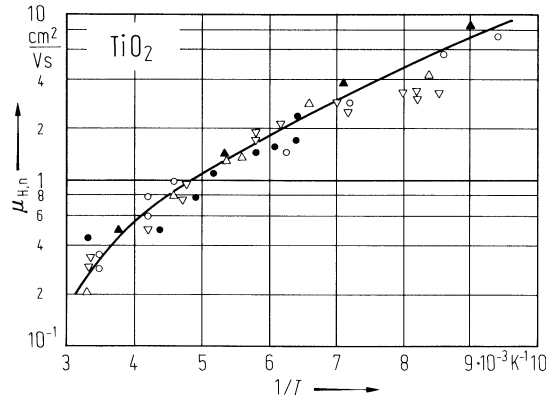


Fig. 4.

TiO₂. Hall mobility vs. temperature at high temperatures for different samples. Curves a: — $\perp c$, --- $\parallel c$ [67B1], curve b: $\perp c$ [69B], curve c: $\parallel c$ [69B], curve d: $\parallel c$ [66B1, 66B2].

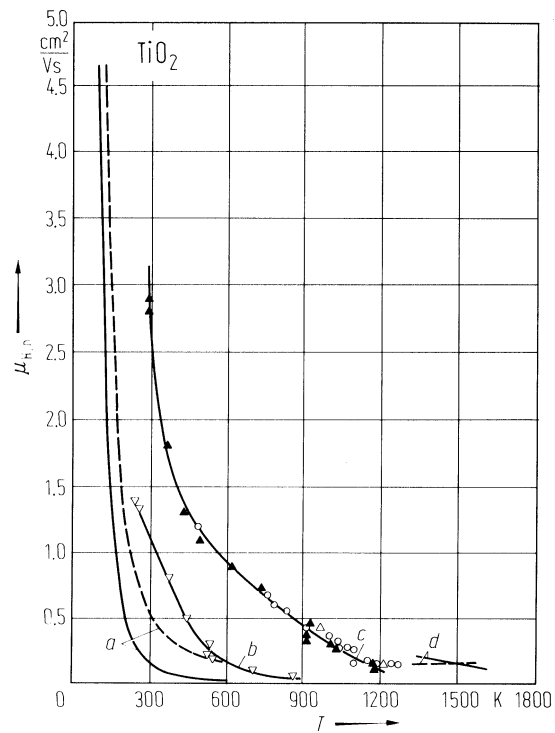


Fig. 5.

TiO₂. Conductivity and static dielectric constant vs. frequency of a reduced rutile single crystal at 300K along [001] direction [68G].

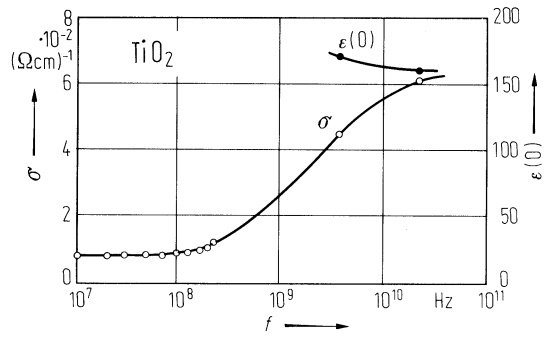


Fig. 6.

TiO₂. Ratio of the Hall coefficients $R_H(\parallel a)$ and $R_H(\parallel c)$ (see tables) for three samples vs. reciprocal temperature. Dashed line: calculated anisotropy based on a two-band model [65B].

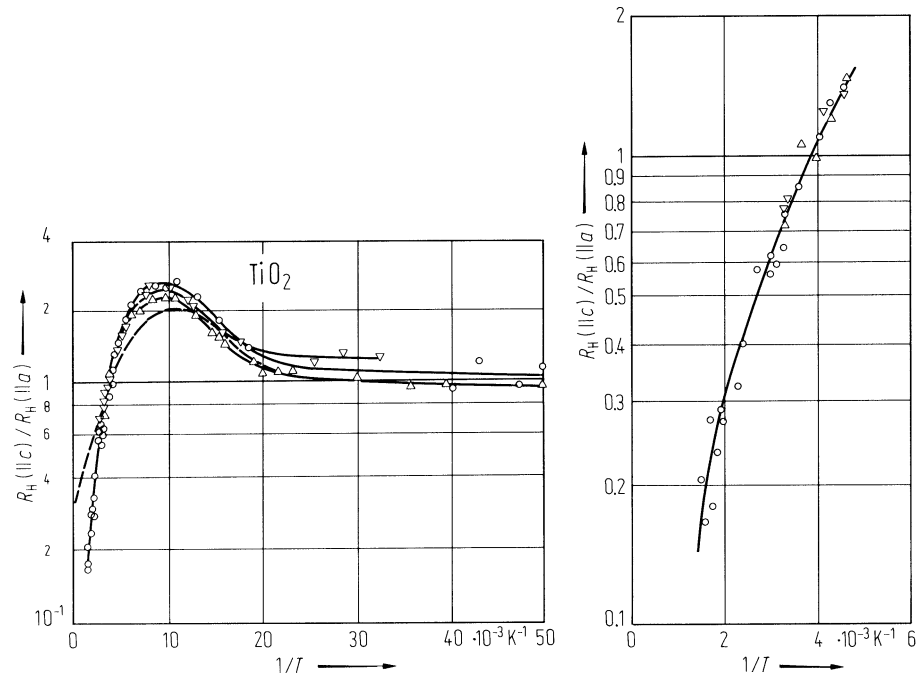


Fig. 7.

TiO₂, rutile. Band structure. Left: Energy vs. wave vector along symmetry lines in the Brillouin zone, right: schematic bands with nomenclature used in

