

substance: $\text{Ti}_n\text{O}_{2n-1}$ ($n \geq 3$)

property: transport properties

conductivity: for Ti_3O_5 : Fig. 1; Ti_4O_7 : Fig. 2, 3; Ti_5O_9 : Fig. 4, 5; Ti_6O_{11} : Fig. 6, 7; Ti_7O_{13} : Fig. 8; Ti_8O_{15} : Fig. 9; Ti_9O_{17} : Fig. 10.

The following table [75H] presents a comparison of calculated and measured values of the conductivity and the carrier mobility, the hopping frequencies f_h and mobilities μ_h and concentrations as well as effective masses of localized (n_{loc}) and delocalized (n_{del}) electrons.

transport parameters

$\sigma_{\text{exp}}[\Omega^{-1} \text{ cm}^{-1}]$	$5.5 \cdot 10^{-3}$	Ti_3O_5	low-temperature phase (see also Figs. 1, 2). $T = 120$ K. σ measured along b -axis of single crystal sample; [77M] gives σ two orders of magnitude lower for Ti_5O_9	69B
	$3.10 \cdot 10^{-3}$	Ti_4O_7		
	6.3	Ti_5O_9		
	$7.0 \cdot 10^{-2}$	Ti_6O_{11}		
	$2.5 \cdot 10^{-1}$	Ti_8O_{15}		
$\sigma_{\text{exp}}[\Omega^{-1} \text{ cm}^{-1}]$	$3.5 \cdot 10^1$	Ti_3O_5	high-temperature phase; $T = 450$ K for Ti_3O_5 and 300 K for the others; [77M] again reports significantly lower conductivity for Ti_5O_9 at 300 K ($\approx 0.6 \Omega^{-1} \text{ cm}^{-1}$)	69B
	$1.5 \cdot 10^3$	Ti_4O_7		
	$5.5 \cdot 10^2$	Ti_5O_9		
	$1.1 \cdot 10^2$	Ti_6O_{11}		
$\mu_{\text{calc}}[\text{cm}^2/\text{V s}]$	0.21	Ti_3O_5	$T = 450$ K	75H
	0.6	Ti_4O_7	$T = 300$ K	
	4.1		$T = 160$ K	
	0.76	Ti_5O_9	$T = 300$ K	
	0.9	Ti_6O_{11}	$T = 300$ K	
$\mu_{\text{exp}}[\text{cm}^2/\text{Vs}]$	1.0	Ti_4O_7	$T = 300$ K	75H
	4.0		$T = 160\text{K}$	
$f_h[\text{Hz}]$	$4.9 \cdot 10^{11}$	Ti_3O_5	$T = 120\text{K}$	75H
	$1.6 \cdot 10^{12}$	Ti_4O_7		
	$9.3 \cdot 10^{12}$	Ti_5O_9		
	$1.4 \cdot 10^{13}$	Ti_6O_{11}		
	$1.5 \cdot 10^{12}$	Ti_8O_{15}		
$\mu_h[\text{cm}^2/\text{V s}]$	$7.0 \cdot 10^{-5}$	Ti_3O_5	$T = 120$ K	75H
	$4.0 \cdot 10^{-6}$	Ti_4O_7		
	$4.2 \cdot 10^{-4}$	Ti_5O_9		
	$2.7 \cdot 10^{-7}$	Ti_6O_{11}		
	$2.1 \cdot 10^{-4}$	Ti_8O_{15}		

$n_{\text{loc}}[\text{cm}^{-3}]$	0.00	Ti ₃ O ₅	high-temperature region, calculated from magnetic susceptibility ($T = 450$ K for Ti ₃ O ₅ and 300 K for the others)	75H
	$1.71 \cdot 10^{21}$	Ti ₄ O ₇		
	$1.10 \cdot 10^{21}$	Ti ₅ O ₉		
	$3.7 \cdot 10^{21}$	Ti ₆ O ₁₁		
	$3.85 \cdot 10^{21}$	Ti ₈ O ₁₅		
$n_{\text{del}}[\text{cm}^{-3}]$	$2.29 \cdot 10^{22}$	Ti ₃ O ₅	high-temperature region, calculated from magnetic susceptibility (T as above)	75H
	$1.54 \cdot 10^{22}$	Ti ₄ O ₇		
	$1.24 \cdot 10^{22}$	Ti ₅ O ₉		
	$7.4 \cdot 10^{21}$	Ti ₆ O ₁₁		
	$4.6 \cdot 10^{21}$	Ti ₈ O ₁₅		
$n_{\text{del}}[\text{cm}^{-3}]$	$9.1 \cdot 10^{20}$	Ti ₃ O ₅	low-temperature region, from EPR data; $T = 120$ K < T_{tr} , except for Ti ₈ O ₁₅ , where no T_{tr} were observed	75H
	$2.4 \cdot 10^{21}$	Ti ₄ O ₇		
	$1.7 \cdot 10^{21}$	Ti ₅ O ₉		
	$3.8 \cdot 10^{21}$	Ti ₆ O ₁₁		
	$5.3 \cdot 10^{21}$	Ti ₈ O ₁₅		
m_{n}/m_0	22.4 (6.7)	Ti ₃ O ₅	high-temperature region, in brackets: low temperature- region defined above	75H
	15.4 (5.6)	Ti ₄ O ₇		
	19.5 (6.4)	Ti ₅ O ₉		
	15.4 (5.4)	Ti ₆ O ₁₁		
	13.2 (12.5)	Ti ₈ O ₁₅		

further transport data and remarks

[76L] finds that σ increases in Ti₄O₇ between 160 and 300 K in a similar way to that reported by [69B] for Ti₅O₉. [83I] reports both types of behaviour depending on the crystal orientation. For one free electron per Ti³⁺ calculated mobilities are 0.55 cm²/V s [69B], 0.05 cm²/V s [76L] at 300 K. Below T_{tr} no activation energies can be obtained for Ti₃O₅, Ti₄O₇, Ti₅O₉, Ti₆O₁₁.

However, Ti₈O₁₅ shows no transition and an activation energy of 0.087 eV. In Ti₃O₅, the transition involves a structural rearrangement in which Ti³⁺ – Ti³⁺ bonds are broken at high temperatures and the electrons become quasi-itinerant. The two transitions seen in Ti₄O₇ and Ti₅O₉ have been ascribed to solid-liquid-gas. The central unit remains a Ti³⁺ – Ti³⁺ bond in the intermediate phase, but this "bipolaron" becomes mobile. The Seebeck coefficient suggests n-type conduction [79S], and in the low-temperature region variable-range hopping occurs [79S]. [83I] reports fine structure in the hysteresis range of Ti₄O₇ (Fig. 3) and three transitions, at 127(2), 132(1) and 139(1) K in the conductivity of Ti₅O₉ (Fig. 5). Unlike [69B], who reports a transition at 130 K in Ti₆O₁₁, [83I] reports two transitions, at 119(1) and 147(1) K (Fig. 7). Interestingly, Ti₇O₁₃ appears to show no metallic region (Fig. 8), but a transition at 115 K↓, 123 K↑ between two semiconducting regions. Below T_{tr} for $n = 5, 6$ or 7, $\ln \sigma$ varies linearly with T , a result ascribed to temperature-dependent incoherent tunneling [83I].

References:

- 69B Bartholomew, R. F., Frankl, D. R.: Phys. Rev. 187 (1969) 828.
- 75H Houlihan, J. F., Danley, W. J., Mulay, L. N.: J. Solid State Chem. 12 (1975) 265.
- 76L Lakkis, S., Schlenker, C., Chakraverty, B. K., Buder, R., Marezio, M.: Phys. Rev. B14 (1976) 1429.
- 77M Marezio, M., Tranquin, D., Lakkis, S., Schlenker, C.: Phys. Rev. B16 (1977) 2811.
- 79S Schlenker, C., Ahmed, S., Buder, R., Gourmala, M.: J. Phys. C12 (1979) 3503.
- 83I Inglis, A. D., LePage, Y., Strobel, P., Hurd, C. M.: J. Phys. C16 (1983) 317.

Fig. 1.

Ti_3O_5 . Conductivity along b -axis vs. (reciprocal) temperature of single crystal material [69B].

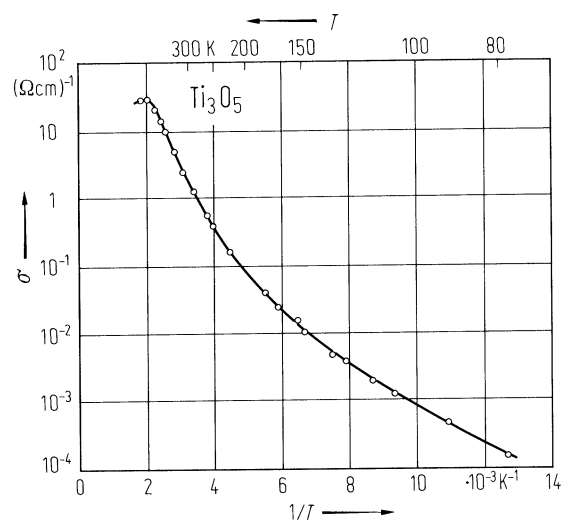


Fig. 2.

Ti_4O_7 . Conductivity along [031] pseudorutile direction vs. (reciprocal) temperature of a single crystal. The inset shows the molar magnetic susceptibility vs. temperature, (χ_m in CGS-emu) [76L].

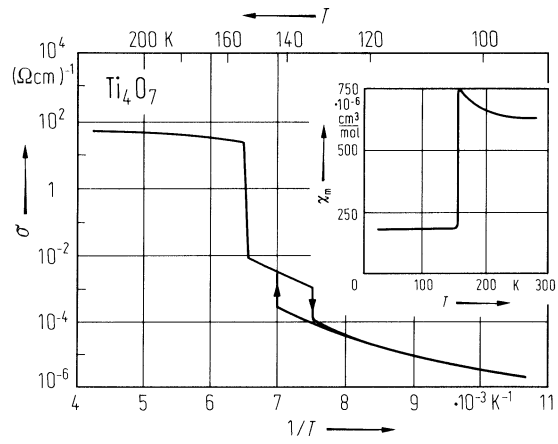


Fig. 3.

Ti_4O_7 . Conductance ($1/R$) vs. temperature, showing fine structure in the hysteresis range. Sample was warmed through the 154 K transition between runs B and C which accounts for the ordinate displacement between the two hysteresis loops. In the as-grown state this sample had an exceptionally low ρ ($\approx 10^{-3} \Omega\text{cm}$) among the samples studied [83I].

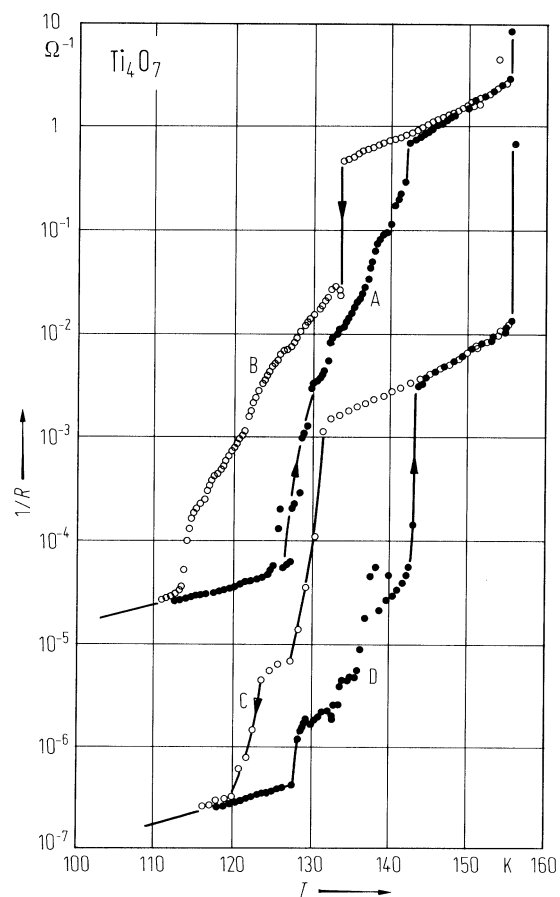


Fig. 4.

Ti_5O_9 . Conductivity vs. reciprocal temperature for a single crystal [77M]. Inset shows transition range on an enlarged scale. Orientation not specified.

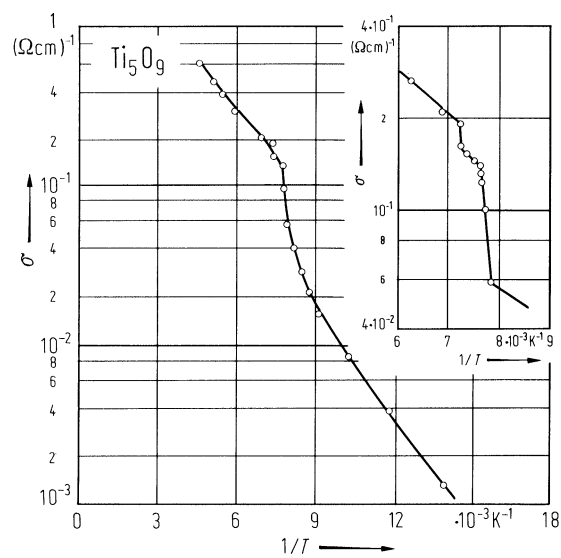


Fig. 5.

Ti_5O_9 . Conductance vs. temperature for a single crystal. (a) shows detail of conductance in the transition region with clearly marked transition temperatures T_1 , T_2 , T_3 ; and (b) shows conductance over a wide temperature range; inset: low temperature range on an expanded scale [83I].

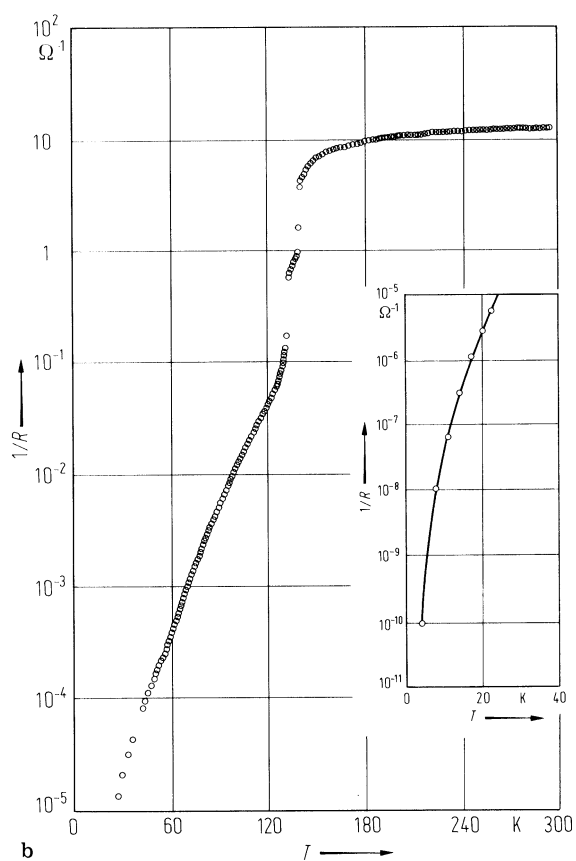
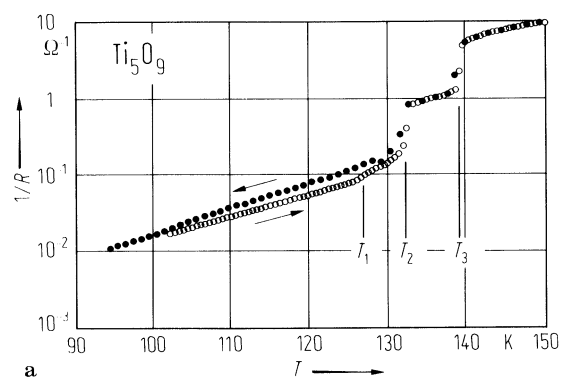


Fig. 6.

Ti₆O₁₁. Conductivity along *b*-axis vs. (reciprocal) temperature for a single crystal [69B].

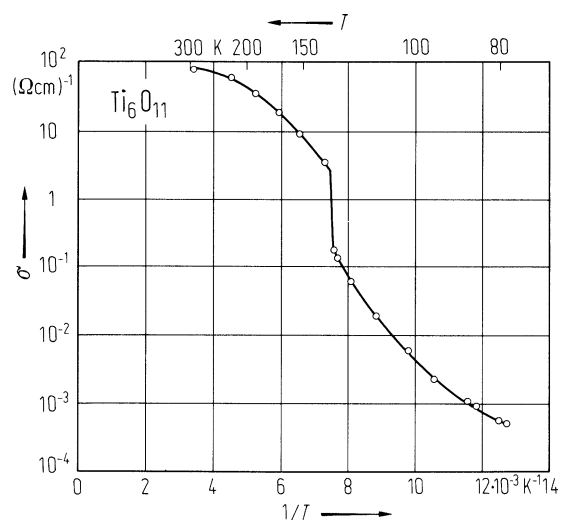


Fig. 7.

Ti_6O_{11} . Conductance vs. temperature. (a) shows detail of conductance in the transition region and (b) shows conductance over a wide temperature range; inset: low temperature range on an expanded scale [83I].

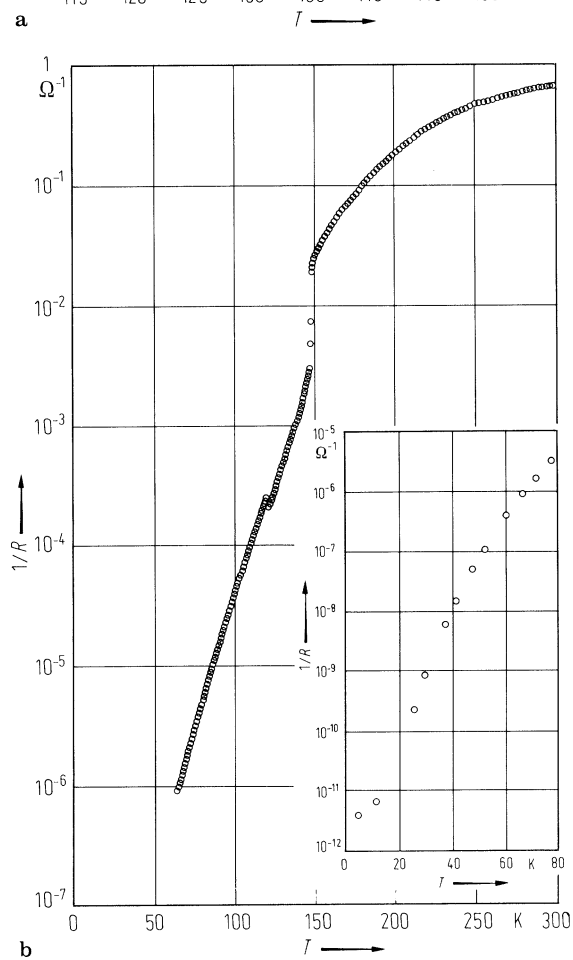
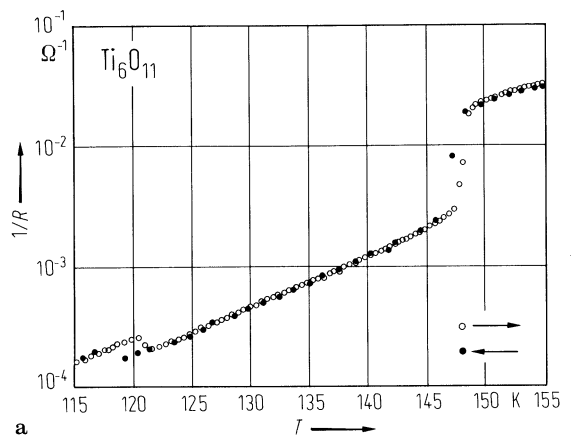


Fig. 8.

Ti_7O_{13} . Conductance vs. temperature. (a) shows detail of conductance in the transition region, (b) shows the conductance over a wide temperature range; inset: low temperature range on an expanded scale [83I].

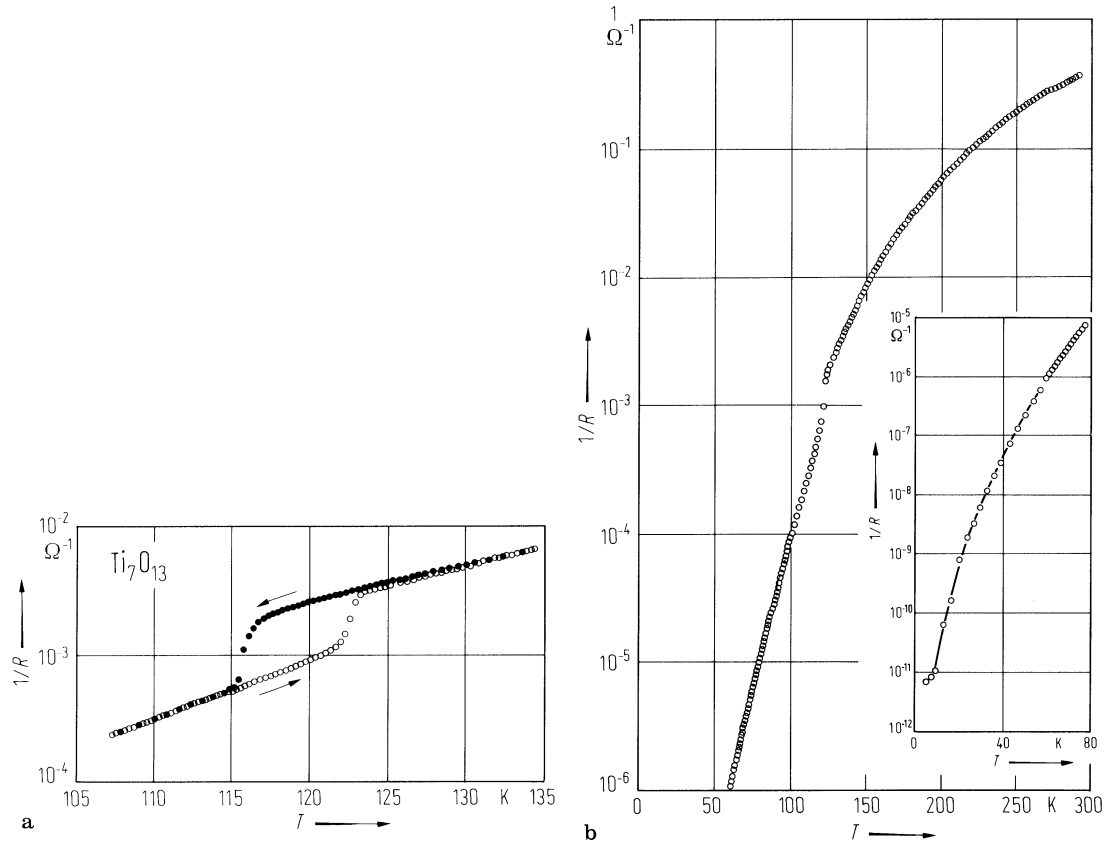


Fig. 9.

Ti_8O_{15} . Conductance vs. temperature. Evidence for a transition at 120 K comes from a discontinuity in $d(1/R)/dT$ at that temperature. Insert shows low temperature range on an expanded scale [83I].

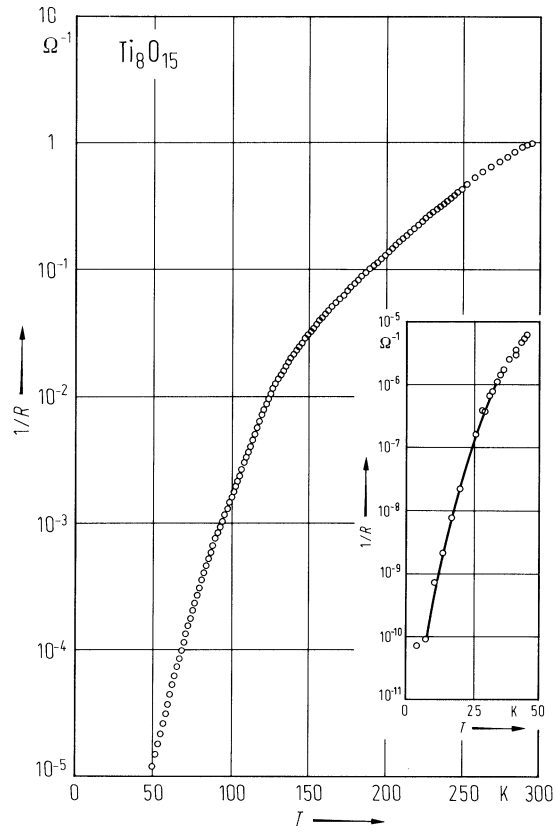


Fig. 10.

Ti₉O₁₇. Conductance vs. temperature. Insert shows low temperature range on an expanded scale [83].

