substance: Ti_nO_{2n-1} ($n \geq 3$)
property: crystal structure of Ti_4O_7

There are two crystallographic transitions at ≈ 150 K and ≈ 130 K on cooling. The lattice parameters only show a first-order transition at 150 K (Fig. 1). Data see below.

crystal structure: room-temperature phase: space group $C_i^1 - A\bar{1}$, $Z = 4$. Rutile-like slabs of TiO_6 octahedra extending infinitely in the *a*- and *b*-directions and 4 octahedra thick in the *c*-direction (Fig. 2).

Two inequivalent strings of Ti ions labelled 3 – 1 – 1 – 3 and 4 – 2 – 2 – 4 can be distinguished at 298 K, though the average Ti – O bond length for the four octahedra are very similar. Below 125 K, a major rearrangement occurs (Fig. 3), characterized by $Ti^{3+} - Ti^{3+}$ homopolar bonding (dimer formation) within the 3 – 1 – 1 – 3 strings. In the intermediate phase, the average interatomic distances differ only slightly from the room-temperature phase, but the thermal factors are anomalously high, consistent with disordering of the dimers (mobile dimers = bipolarons) [80S]. The relationship of the rutile lattice to Ti_4O_7 is shown in Fig. 4.

transition parameters

T_{tr}	154 K (3 K wide)	upper transition	from heat capacity and DTA	74S
ΔH_{tr}	468 (5) cal mol^{-1}			
ΔS_{tr}	3.40(5) cal K^{-1} mol^{-1}			
T_{tr}	142 K↑ (10 K wide)	lower transition		
	130 K↓			
ΔH_{tr}	95(5) cal mol^{-1}			
ΔS_{tr}	0.70(5) cal K^{-1} mol^{-1}			

lattice parameters

a	5.593(1) Å	*T* = 298 K	73M
b	7.125(1) Å		
c	12.456(3) Å		
α	95.02(1)°		
β	95.21(1)°		
γ	108.73(1)°		
a	5.590(1) Å	*T* = 140 K	
b	7.128(1) Å		
c	12.483(2) Å		
α	95.03(1)°		
β	95.34(1)°		
γ	108.89(1)°		
a	5.591(1) Å	*T* = 120 K	73M
b	7.131(1) Å		
c	12.487(2) Å		
α	95.00(1)°		
β	95.33(1)°		
γ	108.88(1)°		

density

d_{calc}	4.32 g cm^{-3}	*T* = 298 K	73M

interatomic distances in TiO_6-octahedra
(in Å (from [73M])

		T = 298 K	140 K	120 K	
Ti(1) –	O(1)	1.940(2)	1.949(4)	2.057(4)	
	O(1)	1.977(2)	2.004(4)	2.058(4)	
	O(2)	1.935(2)	1.936(4)	1.992(4)	
	O(4)	2.041(2)	2.030(4)	2.030(4)	
	O(5)	2.070(2)	2.088(4)	2.037(4)	
	O(6)	2.071(2)	2.058(4)	2.086(4)	
Average			2.006	2.011	2.043	
O(5) –	O(6) $e^{1/3}$	2.694(2)	2.686(6)	2.696(5)	$e^{1/3}$ or $f^{5/8}$ next to an O – O distance
O(5) –	O(4) $e^{1/3}$	2.693(2)	2.745(6)	2.853(6)	indicate that the distance is either
O(5) –	O(2)	2.883(3)	2.904(5)	3.002(5)	a shared edge or part of a shared
O(5) –	O(1)	2.918(2)	2.919(5)	2.920(5)	face, between Ti(1) – Ti(3) and
O(1) –	O(6)	2.834(3)	2.839(6)	2.854(5)	Ti(5) – Ti(8), respectively.
O(1) –	O(4)	3.048(2)	3.038(5)	3.059(5)	
O(1) –	O(2)	2.896(3)	2.893(6)	2.952(6)	
O(1) –	O(1) $e^{1/1}$	2.639(4)	2.659(9)	2.667(8)	
O(2) –	O(4)	2.987(3)	3.009(6)	3.158(6)	
O(2) –	O(1)	2.786(2)	2.784(5)	2.813(5)	
O(5) –	O(4)	2.811(2)	2.804(6)	2.808(5)	
O(5) –	O(1)	2.734(3)	2.723(6)	2.733(6)	
Ti(2) –	O(1)	1.931(2)	1.902(4)	1.776(4)	
	O(2)	1.997(2)	2.001(4)	1.964(4)	
	O(3)	2.010(2)	2.011(4)	1.995(4)	
	O(3)	1.976(2)	1.972(4)	1.958(4)	
	O(4)	2.064(2)	2.068(5)	2.148(4)	
	O(7)	2.061(2)	2.044(4)	1.995(4)	
Average			2.006	2.000	1.973	
O(7) –	O(1)	2.866(2)	2.864(5)	2.845(5)	
O(7) –	O(2) $e^{2/4}$	2.749(2)	2.765(6)	2.700(5)	
O(7) –	O(3)	2.972(2)	2.953(5)	2.936(5)	
O(7) –	O(4) $e^{2/4}$	2.706(2)	2.654(6)	2.566(6)	
O(3) –	O(1)	2.806(3)	2.806(6)	2.772(6)	
O(3) –	O(2)	2.948(2)	2.924(5)	2.921(5)	
O(3) –	O(3) $e^{2/2}$	2.691(3)	2.691(8)	2.547(7)	
O(3) –	O(4)	2.965(2)	2.949(6)	2.897(5)	
O(3) –	O(1)	2.774(2)	2.760(5)	2.725(5)	
O(3) –	O(4)	2.841(2)	2.825(6)	2.770(6)	
O(2) –	O(1)	2.896(2)	2.887(6)	2.840(6)	
O(2) –	O(4)	2.798(2)	2.810(5)	2.791(5)	
Ti(3) –	O(5)	2.156(2)	2.146(4)	2.138(4)	
	O(6)	1.935(2)	1.952(4)	2.049(4)	
	O(7)	2.022(2)	2.039(4)	2.109(4)	
	O(5)	1.994(2)	2.018(4)	2.029(4)	
	O(4)	2.064(2)	2.070(4)	2.037(4)	
	O(3)	1.855(2)	1.862(4)	1.903(4)	
Average			2.004	2.015	2.044	

O(6) –	O(5) $e^{3/1}$	2.694(2)	2.686(6)	2.696(5)
O(6) –	O(7)	2.829(3)	2.845(7)	2.866(7)
O(6) –	O(5)	2.911(2)	2.898(5)	2.896(5)
O(6) –	O(3)	2.872(2)	2.900(5)	2.962(5)
O(4) –	O(5) $f^{3/4}$	2.695(2)	2.670(5)	2.613(5)
O(4) –	O(7) $f^{3/4}$	2.695(2)	2.716(5)	2.752(5)
O(4) –	O(5) $e^{1/3}$	2.693(3)	2.745(6)	2.853(6)
O(4) –	O(3)	3.008(2)	3.033(6)	3.138(6)
O(5) –	O(7) $f^{3/4}$	2.649(2)	2.657(5)	2.644(5)
O(5) –	O(5) $e^{3/3}$	2.601(3)	2.594(8)	2.588(7)
O(3) –	O(7)	3.075(2)	3.103(6)	3.184(6)
O(3) –	O(5)	2.926(2)	2.950(5)	3.042(5)
Ti(4) –	O(4)	2.118(2)	2.117(4)	2.023(4)
	O(2)	1.939(2)	1.934(4)	1.945(4)
	O(7)	1.995(2)	1.985(4)	1.950(4)
	O(7)	2.176(2)	2.190(4)	2.314(4)
	O(6)	1.876(2)	1.882(4)	1.787(4)
	O(5)	2.001(2)	1.967(4)	1.958(4)
Average		2.018	2.012	1.996
O(4) –	O(7) $e^{2/4}$	2.706(2)	2.654(6)	2.566(5)
O(4) –	O(7) $f^{3/4}$	2.695(2)	2.716(5)	2.752(5)
O(4) –	O(6)	3.001(2)	2.993(6)	2.918(5)
O(4) –	O(5) $f^{3/4}$	2.695(2)	2.670(5)	2.613(5)
O(2) –	O(7)	2.897(3)	2.909(5)	2.875(5)
O(2) –	O(7) $e^{2/4}$	2.749(2)	2.765(6)	2.700(5)
O(2) –	O(6)	2.954(2)	2.947(5)	2.936(5)
O(2) –	O(5)	2.868(3)	2.866(7)	2.775(6)
O(7) –	O(7) $e^{4/4}$	2.584(3)	2.571(8)	2.614(8)
O(7) –	O(5) $f^{3/4}$	2.649(2)	2.657(5)	2.644(5)
O(6) –	O(7)	2.948(2)	2.923(5)	2.884(5)
O(6) –	O(5)	3.072(2)	3.062(6)	3.024(6)
Ti(1) –	Ti(1)[a]) edge	2.895(1)	2.926(2)	3.133(2)
	Ti(3)[a])	3.020(1)	2.90(2)	2.802(2)
	Ti(2)[a]) corner	3.604(1)	3.609(1)	3.550(2)
	Ti(2)[a])	3.502(1)	3.491(1)	3.461(1)
	Ti(2)[a])	3.572(1)	3.574(3)	3.465(3)
	Ti(2)[a])	3.553(1)	3.554(3)	3.671(3)
	Ti(4)[a])	3.793(1)	3.783(2)	3.784(2)
	Ti(4)[a])	3.530(1)	3.526(2)	3.534(2)
	Ti(4)[a])	3.425(1)	3.434(2)	3.498(2)
	Ti(3)[b]) edge	3.111(1)	3.124(2)	3.159(2)
	Ti(4)[b]) corner	3.806(1)	3.795(2)	3.699(2)

[a]) Distances inside the rutile blocks.
[b]) Distances between rutile blocks.

Ti(2) –	Ti(2)[a]) edge	2.942(1)	2.937(2)	3.023(2)
	Ti(4)[a])	3.019(1)	3.000(2)	3.083(2)
	Ti(1)[a]) corner	3.604(1)	3.609(1)	3.550(2)
	Ti(1)[a])	3.502(1)	3.481(1)	3.461(1)
	Ti(1)[a])	3.572(1)	3.574(3)	3.465(3)
	Ti(1)[a])	3.553(1)	3.554(3)	3.671(3)
	Ti(3)[a])	3.751(1)	3.746(2)	3.778(1)
	Ti(3)[a])	3.538(1)	3.539(2)	3.557(1)
	Ti(3)[a])	3.464(1)	3.473(2)	3.439(2)
	Ti(4)[b]) edge	3.067(1)	3.101(2)	3.104(1)
	Ti(3)[b]) corner	3.788(1)	3.773(2)	3.765(2)
Ti(3) –	Ti(1)[a]) edge	3.020(1)	2.990(2)	2.802(2)
	Ti(2)[a]) corner	3.751(1)	3.746(2)	3.778(1)
	Ti(2)[a])	3.538(1)	3.339(2)	3.557(1)
	Ti(2)[a])	3.464(1)	3.473(2)	3.493(2)
	Ti(4)[a])	3.556(1)	3.573(2)	3.576(2)
	Ti(4)[a])	3.569(1)	3.555(2)	3.568(2)
	Ti(4)[b]) face	2.811(1)	2.806(1)	2.838(1)
	Ti(4)[b]) corner	3.417(1)	3.434(1)	3.414(1)
	Ti(3)[b]) edge	3.237(1)	3.261(2)	3.267(1)
	Ti(1)[b])	3.111(1)	3.124(2)	3.159(2)
	Ti(2)[b]) corner	3.788(1)	3.773(2)	3.765(2)
Ti(4) –	Ti(2)[a]) edge	3.019(1)	3.000(2)	3.083(2)
	Ti(1)[a]) corner	3.793(1)	3.783(2)	3.784(2)
	Ti(1)[a])	3.530(1)	3.526(2)	3.534(2)
	Ti(1)[a])	3.425(1)	3.434(2)	3.498(2)
	Ti(3)[a])	3.556(1)	3.573(2)	3.576(2)
	Ti(3)[a])	3.569(1)	3.555(2)	3.568(2)
	Ti(3)[b]) face	3.811(1)	2.806(1)	2.838(1)
	Ti(3)[b]) corner	3.417(1)	3.434(1)	3.414(1)
	Ti(4)[b]) edge	3.280(1)	3.295(2)	3.389(2)
	Ti(2)[b])	3.067(1)	3.101(1)	3.104(2)
	Ti(1)[b]) corner	3.806(1)	3.795(2)	3.699(2)

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Fig. 1.

Ti_4O_7. Lattice parameters vs. temperature [70M].

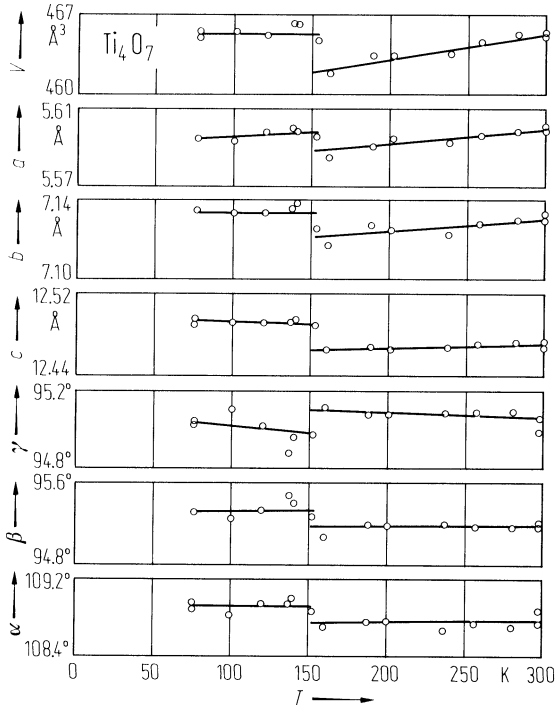

Fig. 2.

Ti_4O_7. Projection of the structure looking down the triclinic *a*-axis at RT [71M].

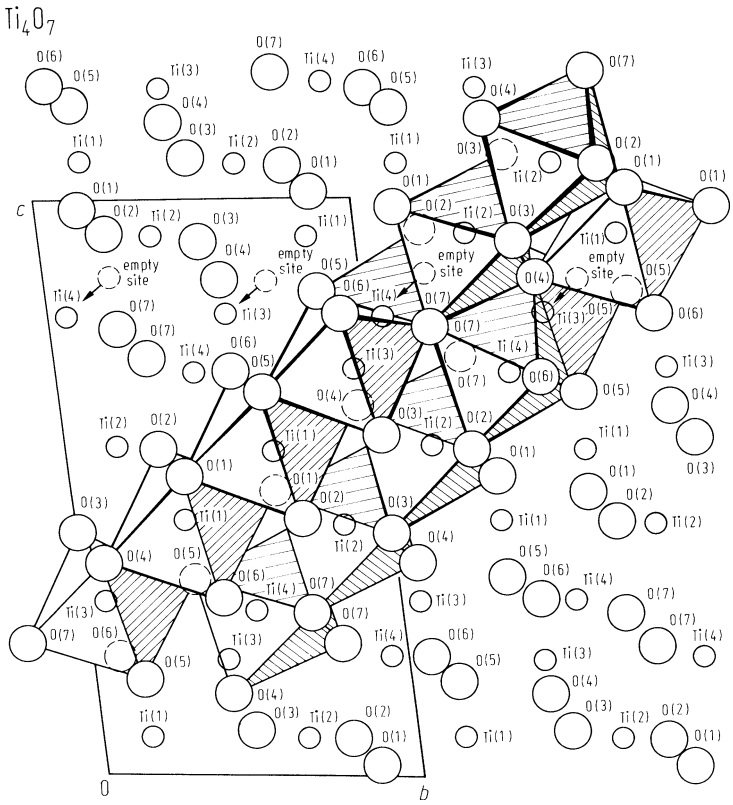

Fig. 3.

Ti_4O_7. (a) Sheets of Ti ions at 298 K. Wavy lines show the shear planes which intersect the paper at an angle of 64º. Inset shows the rutile-derived cell. (b) Same but showing the situation at 125 K [73M].

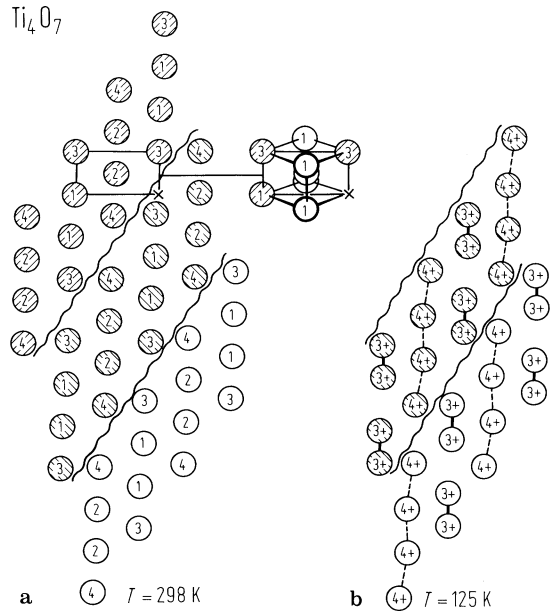

Fig. 4.

Ti_4O_7. Stacking of oxygen octahedra containing Ti in each rutile block. Successive rutile blocks are represented by heavy and light lines. a_R, b_R, c_R represent the pseudorutile cell parameters. Shaded octahedra faces are common between 3-1-1-3 and 4-2-2-4 strings in neighbouring blocks [79H].