substance: VO_2
property: crystal structure, lattice parameters, high temperature phase

This oxide exists in a narrow stoichiometry range $VO_{2-\delta}$ ($\delta < 0.006$) [75B]. Below this stoichiometry, (121)CS planes have been identified [78G]. Intergrowths of V_8O_{15}, or, more rarely, V_9O_{17}, have been observed in slightly reduced material; no phase V_nO_{2n-1} with $n > 10$ has been found [78G]. Values of $\delta < 0$ have also been reported [70K, 74K, 79M].

At ca. 340 K, VO_2 exhibits a metal-semiconductor transition, which is accompanied by a discontinuous transition in other physical properties. Detailed structure: Fig. 1.

crystal structure: tetragonal, space group D_{4h}^{14} – $P4_2/mnm$, $Z = 2$ (subscript R for rutile form)

lattice parameters

a_R	4.5546_3 Å	$T = 360$ K		74M
c_R	2.8514_2 Å			
a_R	4.55396 Å	$T = 360$ K	temperature dependence: Fig. 2	79K
c_R	2.85028 Å			
a_R	4.5555_4 Å	$T = 413$ K		74M
c_R	2.8552_3 Å			
a_R	4.5561_5 Å	$T = 473$ K		
c_R	2.8598_3 Å			
a_R	4.5573_5 Å	$T = 523$ K		
c_R	2.8626_3 Å			
a_R	4.5580_4 Å	$T = 573$ K		
c_R	2.8663_2 Å			

The chains of edge-shared VO_6 octahedra along the *c*-axis in the high-temperature (metallic) phase (Fig. 1) have V – V distances of 2.851 Å across the edge at 350 K and 2.869 Å at 470 K. For V – V across corner, V – V distance is 3.522 Å at 360 K and 3.525 Å at 470 K. Below 340 K, the vanadium ions pair up and rock off the c_R-axis (Fig. 1). Short V – V distance is 2.61914 Å [70L]. The coordination of V becomes very irregular: V – O distances (in Å, $\pm 12 \cdot 10^{-4}$ Å): 1.7628, 1.8633, 1.8935, 2.0149, 2.0241, 2.0637 [70L]. Longer V – V distance: 3.12 Å [56A].

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Fig. 1.

VO_2. Structure and unit cell of (a) monoclinic VO_2, (b) tetragonal VO_2 [78P].

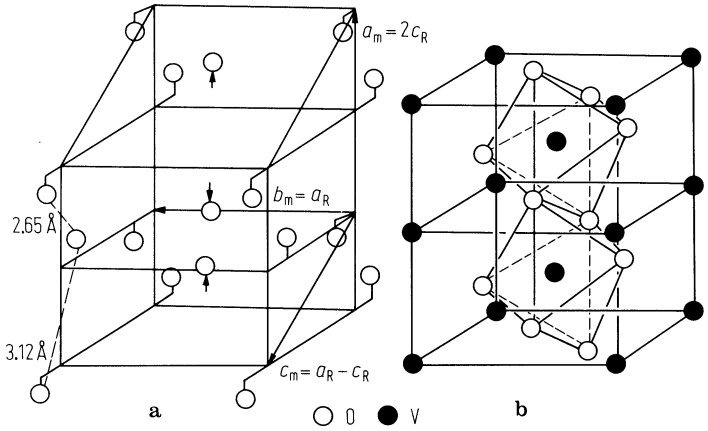

Fig. 2.

VO_2. Lattice parameters vs. temperature. (a) *a*-axis (b) *b*-axis, (c) *c*-axis, (d) angle β [79K].