substance: V_nO_{2n-1}: n ≥ 3
property: crystal structure of V_3O_5

The vanadium-oxygen phase diagram is very complex (Fig. 1 and 2, [63K, 67K, 73K]).

The crystal structure of V_3O_5 is controversial. Space group: C_{2h}^4 – P2/c [80A] or C_{2h}^5 – $P2_1/c$ [76H] at RT and C_{2h}^6 – C2/c above a crystallographic transition temperature T_{tr} = 154.7°C↑, 153.7°C↓ [79A].

lattice parameters

a	10.004 Å	RT		76H
b	5.040 Å			
c	9.854 Å			
β	137.9°			
a	9.859 Å	RT		80A
b	5.0416 Å			
c	6.991 Å			
β	109.478°			
a	9.870 Å	$T \le T_{tr}$	*Z* = 4; for variation with	78C
b	5.052 Å		temperature, see Fig. 3	
c	7.012 Å			
β	109.1°			
V	330.2 Å^3			
a	9.850 Å	$T \ge T_{tr}$	high-temperature phase	78C
b	5.042 Å			
c	7.022 Å			
β	109.3°			
V	329.2 Å^3			
Δ*a*	– 0.13 %	at $T = T_{tr}$		
Δ*b*	– 0.18 %			
Δ*c*	– 0.13 %			

density

d_{calc}	4.720 g cm^{-3}	RT		78C

interatomic distances in the low-temperature phase

[80A]
In the table below, e or f next to an O – O distance means that the distance is a shared edge or part of a shared face, respectively. e or f next to a V – V distance means that the distance is across a shared edge or across a shared face, respectively. Averages in parentheses are corrected for the irregularity of the actual octahedron. Further numbers in parentheses are e.s.d.'s in the least significant digits. Distances are in Å units. RT values.

V(11) octahedron			V(12) octahedron		
V(11) –	O(11)	1.7240(8)	V(12) –	O(12)	1.8912(8)
	O(12)	1.9240 (9)		O(22)	1.9756(9)
	O(21)	1.9638 (9)		O(22)	1.9806(9)
	O(21)	1.9650(9)		O(11)	2.0270(10)
	O(31)	2.0336(9)		O(32)	2.0913(10)
	O(21)	2.1734(8)		O(22)	2.1316(8)
Average		1.9640 (1.9337)	Average		2.0162 (2.0060)
O(21) –	O(21)e	2.578(2)	O(22) –	O(22)e	2.579(2)
O(21) –	O(21)f	2.585(2)	O(22) –	O(22)f	2.566(2)
O(21) –	O(31)f (2×)	2.607(2)	O(22) –	O(32)f (2×)	2.711(2)
O(21) –	O(31)e	2.670(1)	O(22) –	O(32)e	2.670(1)
O(21) –	O(12)e	2.686(1)	O(22) –	O(11)e	2.789(1)
O(21) –	O(12)	2.725(2)	O(22) –	Oil)	2.833(1)
O(11) –	O(12)	2.797(2)	O(12) –	O(11)	2.908(2)
O(21) –	O(11)	2.815(1)	O(22) –	O(12)	2.897(1)
O(21) –	O(12)	2.895(2)	O(22) –	O(11)	3.016(2)
O(11) –	O(31)	2.930(1)	O(12) –	O(32)	3.062(1)
O(21) –	O(11)	2.957(1)	O(22) –	O(12)	3.137(1)
Average		2.738	Average		2.823
V(21) octahedron			V(22) octahedron		
V(21) –	O(12) (2×)	1.9609(8)	V(22) –	O(32) (2×)	1.9815(7)
	O(31) (2×)	2.0249(7)		O(22) (2×)	1.9954(9)
	O(21) (2×)	2.0392(9)		O(11) (2×)	2.0414(8)
Average		2.0083 (2.0064)	Average		2.0061 (2.0051)
O(21) –	O(31)e (2×)	2.670(1)	O(22) –	O(32)e (2×)	2.670(1)
O(21) –	O(12)e (2×)	2.686(1)	O(22) –	O(11)e (2×)	2.789(1)
O(12) –	O(31) (2×)	2.793(1)	O(11) –	O(32) (2×)	2.842(1)
O(12) –	O(31) (2×)	2.844(1)	O(11) –	O(32) (2×)	2.848(1)
O(12) –	O(21) (2×)	2.965(2)	O(11) –	O(22) (2×)	2.919(2)
O(21) –	O(31) (2×)	3.064(2)	O(22) –	O(32) (2×)	2.948(2)
Average		2.837	Average		2.836
V – V distances					
V(11) –	V(11)f	2.8171(4)	V(12) –	V(12)f	2.7632(4)
V(11) –	V(21)e	2.9708(3)	V(12) –	V(22)e	2.9730(3)
V(11) –	V(21)e	3.0239(3)	V(12) –	V(22)e	3.0020(3)
V(11) –	V(11)e	3.2438(4)	V(12) –	V(12)e	3.2067(4)

The structure is based on a shear plane (see Fig. 4). Four quite different octahedra are found at low temperatures as seen in the table above. The vanadium octahedra are shown in Fig. 5; partial charges calculated are (in units of *e*) V(11) 3.86, V(12) 3.02, V(21) 3.06, V(22) 3.07.

At the transition, the different octahedral coordinations of V^{III} inside the shear planes become equivalent, and the vanadiums at the shear-phase edges also become equivalent. Thus, if subscript s denotes an atom at the shear

plane, low-temperature V_3O_5 can be formulated as $(V^{IV})_s(V^{III})_s(V_{1/2}{}^{III},V_{1/2}{}^{III})O_5$ and the hightemperature form as $(V^{IV},V^{III})_s(V^{III})O_5$.

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Fig. 1.

VO_x. Phase diagram over the range V_2O_3 to V_2O_5, [63K, 67K, 73K].

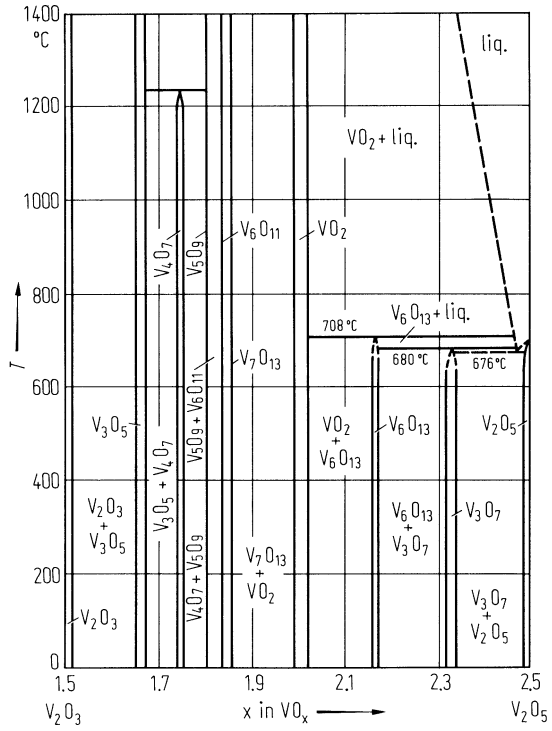

Fig. 2.

VO_x. Phase diagram in the V_2O_3–VO_2 range with oxygen isobars [63K, 67K, 73K].

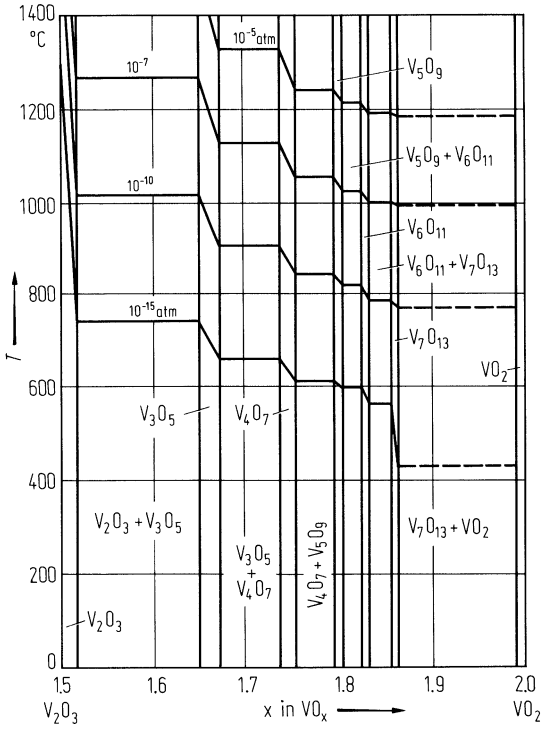

Fig. 3.

V_3O_5. Lattice parameters vs. temperature [76K].

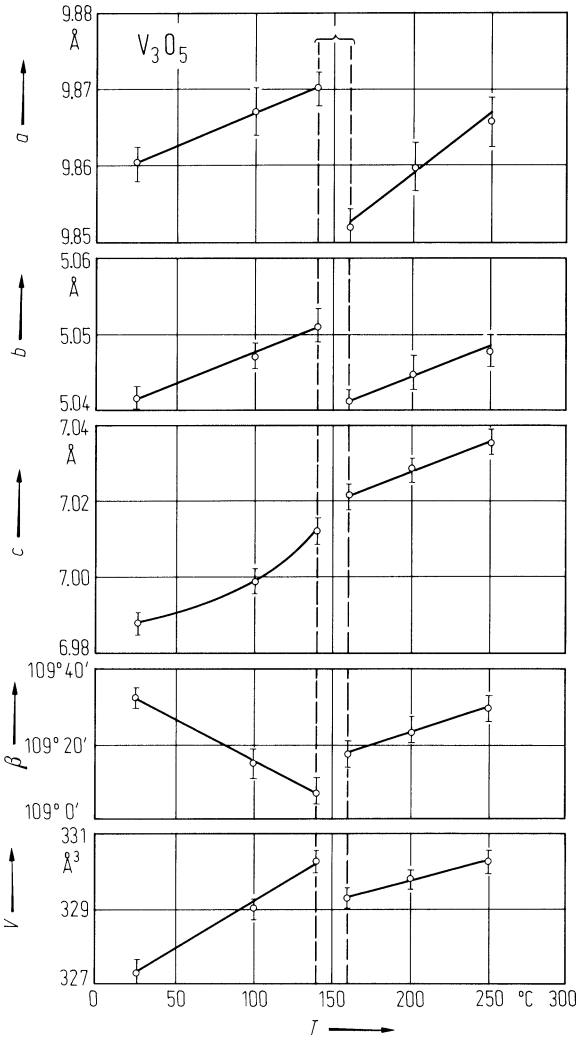

Fig. 4.

V_3O_5. Projection of the structure on [0 1 0] [80A]. Unit cell indicated by dotted line.

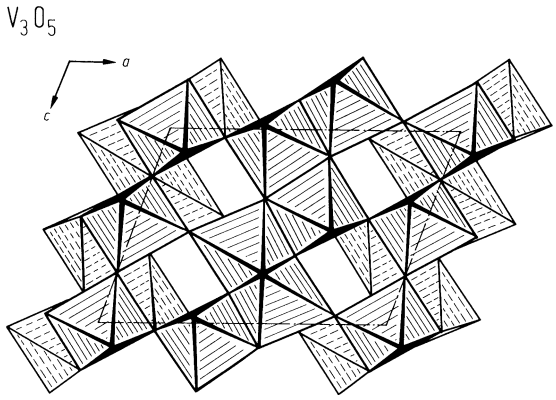

Fig. 5.

V_3O_5. Vanadium octahedra: (a) tetravalent V-atom V(11), (b) trivalent V-atom V(12), (c) trivalent V- atom V(21), (d) trivalent V-atom V(22) [80A]. Distances in Å.