substance: WO_3
property: structural data of tetragonal WO_3

space group D_{4h}^7 – P4/nmm, Z = 2. Four O-atoms lie in a plane and one each above and below the W-atoms, which are themselves displaced some 0.06 c (= 0.23 Å) out of the O_4 plane; see Fig. 1.

lattice parameters and linear thermal expansion

a	5.191(2) Å	T = 740°C	75S
c	3.858 Å		
α_a	$2.33 \cdot 10^{-5}$ K^{-1}	T = 770...950°C	52K
α_c	$7.1 \cdot 10^{-6}$ K^{-1}		

parameters of the phase transitions

α-WO_3 to β-WO_3: first order transition showing considerable hysteresis

$T_{tr}\downarrow$	– 40°C	X-ray	60T
	– 50°C	domain structure	52H
	– 55°C	dilatometry	49F
	– 40°C	single crystal, conductivity	65C
	– 43°C	single crystal, conductivity	70B
$T_{tr}\uparrow$	– 25°C	X-ray	60T
	– 10°C	domain structure	52H
	– 15°C	dilatometry	49F
	– 22°C	single crystal, conductivity	65C
	– 23°C	single crystal, conductivity	70B
ΔH_{tr}	39 cal mol^{-1}		70B
	38(2) cal mol^{-1}		76C
ΔS_{tr}	0.16 cal K^{-1} mol^{-1}		70B
	0.154 cal K^{-1} mol^{-1}		76C

β-WO_3 to γ-WO_3:

T_{tr}↓	9°C	single crystal, conductivity	70B
	1°C	polycrystalline, conductivity	
	10°C	single crystal, conductivity + Hall effect	65C
	– 15°C	conductivity	72H
	– 19°C	microwave reflectivity	
T_{tr}↑	25...35°C	single crystal, conductivity	70B
	21...40°C	polycrystalline, conductivity	
	27°C	single crystal, conductivity + Hall effect	65C
	17°C	conductivity	72H
	0°C	microwave reflectivity	
ΔH_{tr}	20 cal mol^{-1}		70B
	19(2) cal mol^{-1}		76C
ΔS_{tr}	0.07 cal K^{-1} mol^{-1}		70B
	0.064(6) cal K^{-1} mol^{-1}		76C

The transition temperature for substoichiometric WO_{3-x} is lower; for $x = 9 \cdot 10^{-5}$ T_{tr} is about 2°C lower and $\Delta H_{tr} \approx 8.5$ cal mol^{-1}. For $x \geq 2 \cdot 10^{-4}$ the transition from the γ-form to the β-form is suppressed.

γ-WO_3 to orthorhombic WO_3: the transition occurs at 330°C [59S], though the monoclinic angle β only becomes 90° at a higher temperature (467°C) [75S].

T_{tr}	330°C	dilatometry	the transition is at least of	51S
	330°C	heat capacity	second order; for variation of	56S1
	339°C	resistivity	lattice parameters, see Fig. 2	76C
	330°C	resistivity		59S, 63C
	335°C	resistivity		58F
ΔH_{tr}	330 cal mol^{-1}			56S1
	7(1) cal mol^{-1}			76C
ΔS_{tr}	0.55 cal K^{-1} mol^{-1}			56S1
	0.011 cal K^{-1} mol^{-1}			76C

orthorhombic to tetragonal WO_3: the transition appears higher than second order and over a wide temperature range both forms coexist. For a structural model, see Fig. 3

T_{tr}	710...770°C	X-ray diffraction	70A
	750°C	X-ray diffraction	66R
	740°C	X-ray diffraction	51S
	755°C	dilatometry	51S
	740°C	single crystal expansion	56S2, 55H
	730°C	heat capacity	51S, 56S1
ΔH_{tr}	450 cal mol^{-1}		51S,
ΔS_{tr}	0.45 cal K^{-1} mol^{-1}		56S1, 58F

The systematics of these transitions have been explained in terms of the condensation of soft phonon modes at the points Γ, X, M and R of the Brillouin zone of the hypothetical cubic form (O_h^1 – Pm3m) and the P, Z, M and A points in the tetragonal (D_{4h}^7 – P4/nmm) prototype. The condensed modes are

monoclinic low-temperature phase (C_s^2 – Pc): 80H

W	$\Gamma_{15}^z + +M'_3{}^z +(X_5^z)^x + (X_5^z)^y$
O	$(R_{25}^x + R_{25}^y + R_{25}^z)$

triclinic phase (C_i^1 – $P\bar{1}$): 80H

W	$M'_3{}^z + (X_5^x)^y$
O	$(R_{25}^x + R_{25}^y + R_{25}^z)$

monoclinic high-temperature phase (C_{2h}^5 – $P2_1/c$): 80H

W	$M'_3{}^z + (X_5^x)^y$
O	$(R_{25}^x + M_3^y + R_{25}^z)$

orthorhombic phase (D_{2h}^{16} – Pmnb): 80H

W	$M'_3{}^z + (X_5^x)^y$
O	$M'_3{}^z + (M'_5{}^y)^z + 2(X_5^x)^y$

tetragonal phase (D_{4h}^7 – P4/nmm): 80H

W	$M'_3{}^z$
O	$M'_3{}^z$

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Fig. 1.

WO_3 (tetragonal). (a) Projection of the oxygens at $z = 0$ and the tungstens at $z = \pm 0.06$ onto the basal plane, (b) projection onto the x–0–z face; lattice parameters at $T = 770^{o}$C [52K].

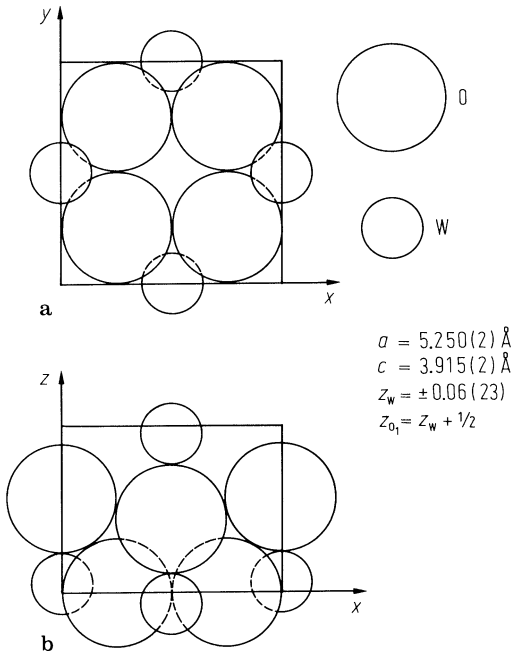

Fig. 2.

WO_3. Lattice parameters and interplanar spacings vs. temperature for various samples [70A]. The crystal symmetry is monoclinic between 17 and 330ºC and orthorhombic between 330 and 740ºC (see tables). The unique angle β is, however close to 90º in the monoclinic phase (90.91º at RT), and *a*, *b*, *c* were calculated as if the crystal were orthorhombic even below 330ºC.

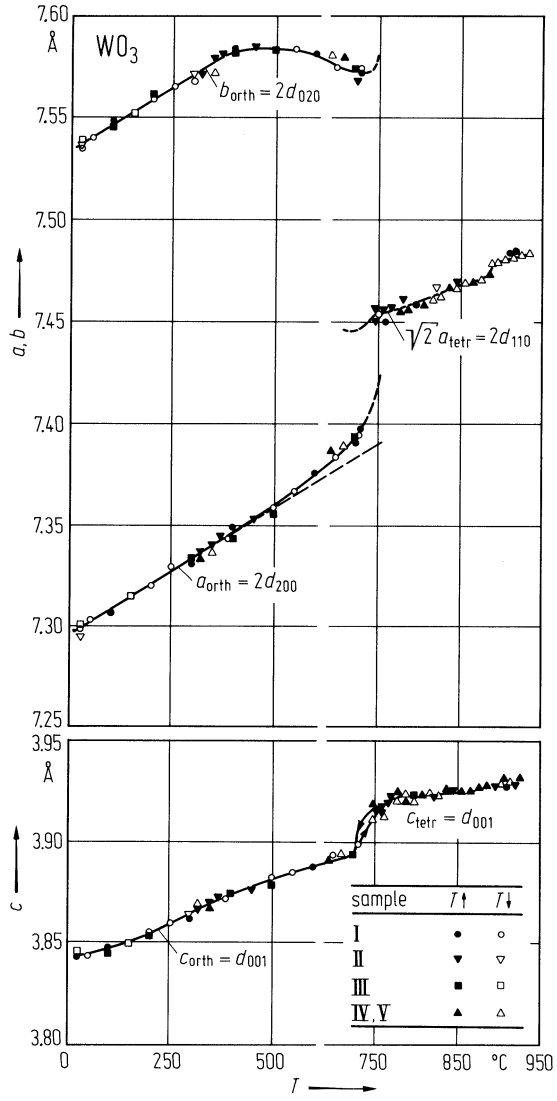

Fig. 3.

WO_3. Model for the orthorhombic-tetragonal distortion [70A]. W^+, W^- are W atoms above and below the O-plane.