

Tableau 5. *Distances intermoléculaires* < 4 Å

S—C'(3)	3,87 (1)	C(3)—C'(3)	3,52 (2)
S—C'(4)	3,65 (1)	C(3)—C'(4)	3,53 (2)
O—C'(4)	3,94 (1)	C(4)—C'(4)	3,77 (2)
O—C'(5)	3,81 (1)	C(4)—C'(7)	3,79 (2)
O—C'(8)	3,78 (1)	C(5)—C'(5)	3,82 (2)
O—C''(8)	3,62 (1)	C(5)—C'(6)	3,60 (2)
C(2)—C'(2)	3,92 (2)	C(5)—C'(7)	3,69 (2)
C(2)—C'(3)	3,72 (2)	C(6)—C'(6)	3,74 (2)
C(2)—C'(4)	3,89 (2)	C(6)—C''(6)	3,75 (2)
C(2)—C'(8)	3,85 (2)	C(6)—C'(7)	3,84 (2)
N—C'(4)	3,56 (1)	C(6)—C'(8)	3,84 (2)
N—C'(5)	3,96 (1)	C(7)—C'(8)	3,74 (2)

ridine sont obtenues avec les cycles azotés les plus symétriques.

L'examen des distances intermoléculaires inférieures à 4 Å (Tableau 5) montre que la cohésion de la struc-

ture cristalline est assurée par des contacts de van der Waals.

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The Orthorhombic Phase of WO₃

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Abstract. From *ca* 467 to 680°C WO₃ exhibits orthorhombic symmetry. The structure is perovskite-like with space group *Pmnb* and *a* = 7.341 (4), *b* = 7.570 (4), *c* = 7.754 (4) Å. The deviation from the ideal perovskite structure is characterized by a zigzag motion of the W position in the **b** and **c** directions as well as a tilt system with tilt angles around **a**. The relation with other WO₃ phases is discussed.

Introduction. WO₃ has been studied in detail because of its ferroelectric, electrooptic, and semiconducting properties. It also shows the ability to incorporate metals, ammonium ions, and hydrogen to form tungsten bronzes, and displays colour centres on irradiation with UV light, application of an electrical field or doping with protons of high mobility. Unfortunately it is very difficult to obtain good single crystals as WO₃ shows a tendency to form substoichiometric shear phases (Sundberg & Tilley, 1974). Hence detailed structural data are lacking.

The crystals show five phase transitions in the range –180 to 900°C changing from tetragonal–orthorhombic–monoclinic–triclinic–monoclinic during cooling (Tanisaki, 1960*a*; Salje & Viswanathan, 1975). At room temperature a monoclinic (WO₃ I) and a triclinic

(WO₃ II) modification can be obtained. Only the structures of the monoclinic phase at room temperature (Tanisaki, 1960*b*; Loopstra & Rietveld, 1969) and at –70°C (WO₃ II) (Salje, 1976*b*) have been determined. In this paper the structure of the orthorhombic phase is described and compared with the structures of the monoclinic and tetragonal varieties. The structure of the triclinic phase will be reported later.

The preparation of single crystals of WO₃ has been described (Salje & Viswanathan, 1975). For the X-ray investigations only thin plates of WO₃ (II) with pseudo-orthorhombic morphology were used. The same crystals were used in all other experiments (Salje, 1974). They show no domain structures. From the results of Berak & Sienko (1970) it can be assumed that these crystals are stoichiometric although the best single crystals show the triclinic and not the monoclinic phase at room temperature. They differ from those we obtained by gas transport. These varieties are similar to those described by Schröder & Felser (1972) and always show domain structures.

The crystals were mounted on a Ni wire which was screwed on the top of a goniometer head. The heating element was bent to form a U with the crystal at the bottom. The probe was spliced with 'Leitsilber' (Fa.

Demetron Nr. 245/6200 3100). This material is plastic for the first five minutes, during which the orientation of the crystal can be corrected. Later the probe was dried for 6 h at room temperature and then for 3 h at temperatures well above 120°C. After this treatment the crystal is held firmly and there is good contact between the crystal and wire. The probes can be heated to more than 850°C without much disorientation of the crystal. Unfortunately, diffuse streaks occur on the X-ray photographs due to the mounting material.

Before photographs of the high-temperature orthorhombic modification could be taken it was necessary to produce good crystals of the monoclinic variety (WO₃ I) by heating and subsequent cooling of the triclinic crystals (WO₃ II) (Salje & Viswanathan, 1975). This was carried out by orienting the triclinic crystals at room temperature and then heating them to *ca* 350°C. The orientation was corrected if necessary. On cooling, the monoclinic phase appears uniformly. The crystal was twinned along [100]. The reflexions of the single individuals are superposed in *a** and *b**. The *c** axis is split with nearly the same intensity for both parts. Photographs of the twinned monoclinic crystals were taken at room temperature. Only the *h*0*l*, 0*kl* (precession camera) and *hk*0 (Weissenberg camera) layers were used. Subsequently the crystals were heated again and the changes in the intensities were observed up to 600°C by taking Weissenberg photographs. With the crystal at this temperature it was remounted on the precession camera and the *h*0*l* and 0*kl* layers were again photographed. In this way the intensity factors I_{600}/I_{20} were derived for all reflexions. With this method irregular effects due to broadening of the reflexions and streaks, identical in both phases, have been largely eliminated.

The intensity factors contain the Debye temperature factor and also effects due to structural changes. The room-temperature structure was solved by Tanisaki (1960*b*) by X-ray methods and refined by Loopstra & Rietveld (1969) from neutron data. As the principal result of Tanisaki was correct his calculated $|F|$ values were used. They were multiplied by the square root of the determined intensity factor of each reflexion. The refinement converged rapidly to $R = 6.1\%$. No attempt was made to refine further, as the error is due to the poor reflexions in the *h*0*l* layer in which the spots are split because of twinning at room temperature. For low *h*0*l* values the twinned individuals cannot be separated and compared with the intensities of the untwinned orthorhombic phase.

The space group is *Pmnb* with $a = 7.341(4)$, $b = 7.570(4)$, $c = 7.754(4)$ Å (Salje & Viswanathan, 1975). In the reorientation of this cell given by Schröder (1976) the values for *a* and *b* were interchanged erroneously.

The atomic parameters are given in Table 1 with maximum standard deviations of 0.001 (W) and 0.01

Table 1. Refined atomic parameters and interatomic distances (Å) of orthorhombic WO₃

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
W(1)	0.25	0.029	0.031	0.58
W(2)	0.25	0.030	0.532	1.27
O(1)	0	0	0	
O(1')	0.5	0	0	
O(2)	0	0	0.5	
O(2')	0.5	0.5	0	
O(3)	0.25	0.269	0.027	
O(4)	0.25	0.278	0.471	
O(5)	0.25	0.004	0.262	
O(6)	0.25	0.015	0.776	
W(1)—O(1)	1.86	W(2)—O(2)	1.87	
W(1)—O(1')	1.86	W(2)—O(2')	1.87	
W(1)—O(3)	1.81	W(2)—O(3)	2.03	
W(1)—O(4)	1.91	W(2)—O(4)	1.94	
W(1)—O(5)	1.81	W(2)—O(5)	2.10	
W(1)—O(6)	1.98	W(2)—O(6)	1.89	

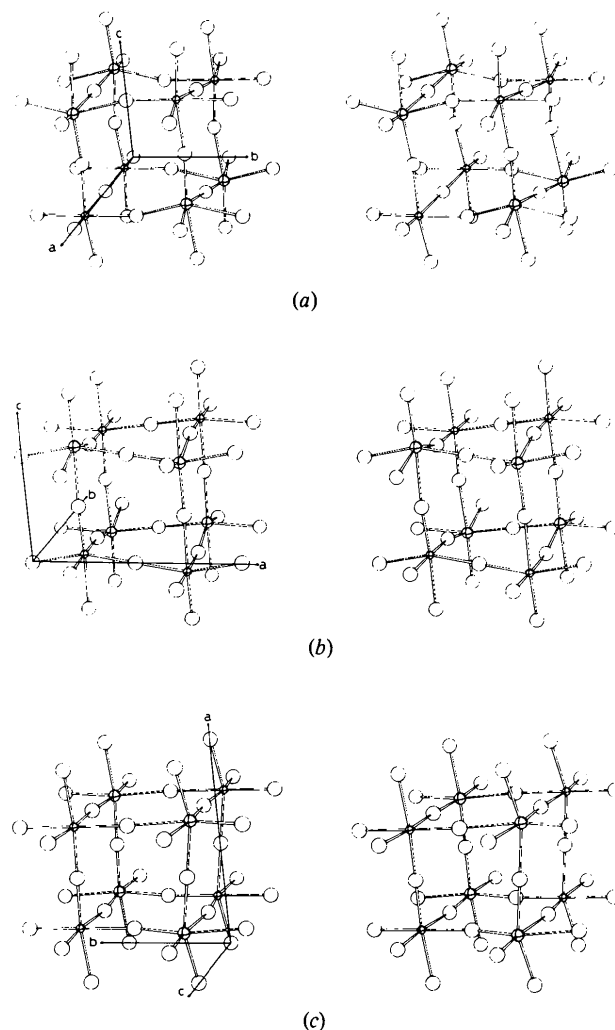


Fig. 1. Structure of orthorhombic WO₃.

(O). The B values of O have not been refined and were set to 2 \AA^2 . From a comparison of positional coordinates given by Tanisaki (1960*b*) and Loopstra & Rietveld (1969) it can be seen that the O positions have not been exactly determined. As the data of Tanisaki are used for this analysis, further refinement would seem to be useful. This will be carried out and reported together with the structure of the triclinic phase. The orthorhombic structure is shown in Fig. 1.*

Discussion. WO_3 exhibits a perovskite-like structure even in the orthorhombic phase. The octahedra are somewhat deformed and tilted. The W positions deviate from the midpoints of the octahedra to form zigzag chains in the b and c directions. The deformation waves are coherent and give rise to deformation amplitudes approximately in $[011]$. The structure is entirely different from that proposed by Schröder (1976), which is based on edge-sharing octahedra.

From a knowledge of this structure the phase transition can be discussed on the basis of the concept of 'critical modes' (Salje, 1976*a*). The additional effects of shear structures are very common in WO_3 and affect the phase transition temperatures. Nevertheless they are unimportant for the occurrence of the phase transition.

In WO_3 , as in most perovskite-like structures, two principal sets of critical modes appear, the generalized

Slater and torsional (R_{25}) modes. The torsional modes give rise to tilt structures (Glazer, 1972). Slater modes induce deformation of the individual octahedra and cause a displacement of the 'central' positions. The ideal structure ($Pm3m$) was not observed in WO_3 . The highest symmetric form is realized in the tetragonal phase with space group $P4/nmm$ (Kehl, Hay & Wahl, 1952). This phase is defined by a hypothetical soft mode (A_{1g}) in the M point on the zone boundary of the cubic phase (Salje, 1975; Zak, 1969). It induces a zigzag motion of the W positions as shown in Fig. 2. Only one zone boundary mode of the Slater type is critical. At a lower temperature the orthorhombic phase becomes stable. The phase transition near 680°C can be explained by freezing an additional critical mode with normal coordinates parallel to $[010]$. This mode corresponds to another M -phonon in the Brillouin zone of the tetragonal phase. From this a doubling of the unit cell according to $a' = \sqrt{2}a$ and $b' = \sqrt{2}b$ occurs. Furthermore, a torsional mode must be critical. This mode can hardly be seen in the X-ray experiments

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32166 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

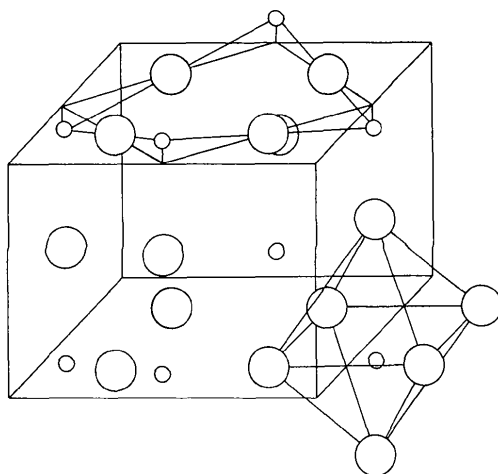


Fig. 2. Deformation structure of tetragonal WO_3 . The W positions are shifted from the octahedra midpoints to form zigzag chains along $[110]$.

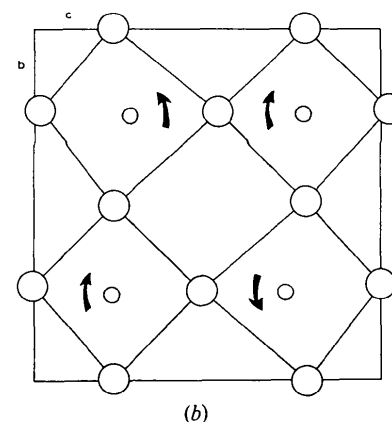
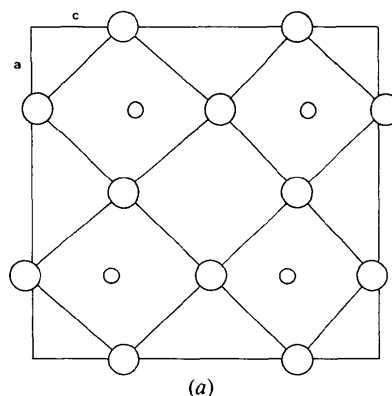


Fig. 3. Projections of the structure of orthorhombic WO_3 .

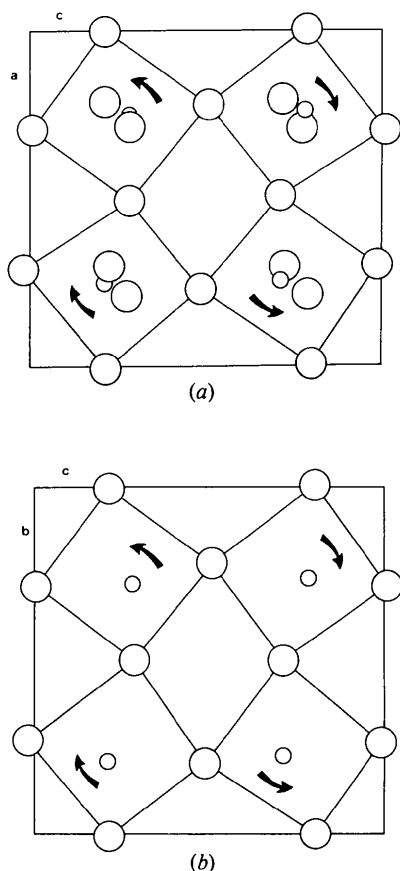


Fig. 4. Tilt structure of monoclinic WO_3 at room temperature.

because the normal coordinates mainly affect the O positions. This mode generates a tilt structure with $c' = 2c$ (Fig. 3). The tilt axes are parallel to **a**.

In the room-temperature phase another torsional mode in the ab plane becomes weak with tilt axes along **c** (Fig. 4b). The critical behaviour of a torsional mode alone is mainly correlated with a second-order phase transition (e.g. SrTiO_3). The critical parameter is the tilt angle. From this point of view the orthorhombic phase is the ordered phase of the monoclinic room-temperature phase with respect to the tilt motion along [001].

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