

The Thermal Expansion and Phase Transitions of WO_3 *

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The thermal expansion of WO_3 from room temperature to 700°C . has been measured by X-ray diffraction methods. The expansion of the a and c axes of the unit cell can be represented by a smooth curve for the entire range investigated. The b axis expands uniformly from room temperature to about 300°C . and decreases slightly in length from 330 to 700°C . The monoclinic unit cell undergoes a transformation near 330°C . to an orthogonal form, which is probably orthorhombic.

Foëx (1945) measured the thermal expansion of WO_3 dilatometrically and reported an average coefficient of linear expansion of about 13×10^{-6} from room temperature up to about 330°C .; the coefficient decreased to 10×10^{-6} for the range from 330° to 710°C . (these values were estimated from Foëx's graphical data).

A somewhat different picture of the thermal expansion of WO_3 was given by Ueda & Ichinokawa (1951); on the basis of high-temperature X-ray diffraction measurements, they reported that all three axes of the 'orthorhombic' unit cell expand linearly and uniformly up to about 710°C ., where an abrupt change to tetragonal symmetry takes place.

It is generally agreed that above 710°C . WO_3 has a simple tetragonal structure (Ueda & Ichinokawa, 1951; Kehl, Hay & Wahl, 1952). There has been considerable disagreement, however, concerning the room-temperature structure. Braekken (1931) has reported that the unit cell is triclinic (pseudo monoclinic) with all angles close to 90° . The unit cell was subsequently described as monoclinic by Magnéli (1949), orthorhombic by Ueda & Ichinokawa (1951) and triclinic by Wyart & Foëx (1951). Recently, a detailed single-crystal and powder study by Andersson (1953) established that the unit cell is monoclinic (pseudo orthorhombic) with

$$a = 7.285, \quad b = 7.517, \quad c = 3.835 \text{ \AA}, \quad \beta = 90.9^\circ.$$

In the present investigation, for which only powdered specimens were available,‡ it was found that, using ordinary film techniques, it was very difficult to rule out any of the three suggested crystal systems. When a Geiger-counter diffractometer with its superior resolution and relative freedom from absorption errors

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‡ Specimens of purified WO_3 from two sources, A. D. Mackay Inc., and Fisher Scientific Co., were used. No significant differences in behavior were observed between the two.

was used, it became clear that the unit cell was not orthorhombic. Several reflections of the type $hkl/hk\bar{l}$, which appeared on films as broad lines, were resolved into doublets on diffractometer traces. The diffractometer data were indexed satisfactorily on the basis of the monoclinic unit cell proposed by Andersson (1953) and Magnéli (1949).

In the course of an investigation of the thermal expansion of various cubic sodium tungsten bronzes (compounds of the general formula Na_xWO_3 , where x varies from 0.3 to about 0.95), an accurate knowledge of the coefficients of expansion of WO_3 from room temperature to about 650°C . was required. A high

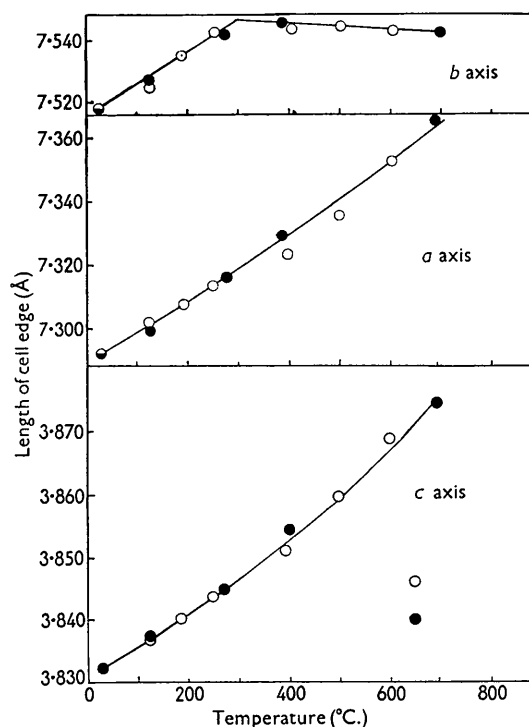


Fig. 1. Thermal expansion of WO_3 (25– 700°C). Open circles: sample from A. D. Mackay Inc.; closed circles: sample from Fisher Scientific Co.

temperature X-ray diffraction study of the compound was undertaken. A small flat-surfaced heater, consisting of nichrome heating coils imbedded in alundum cement, was mounted on the goniometer shaft of a Norelco high-angle diffractometer in place of the usual specimen holder. The specimen, in the form of a finely ground powder, was sprinkled onto a thin flat platinum disk, about 1 cm. square, which was in turn mounted on the upper flat surface of the heater. A thermocouple, welded to the surface of the platinum disk, was used for temperature measurement. Thermocouple measurements were calibrated by plotting thermocouple voltages against melting points of several substances melted on the specimen holder.

The results of the measurements of the thermal expansion of the three unit cell axes are shown in Fig. 1. The values shown are based on measurements of peak locations in the range from 20° to about 60° (2θ). Peaks at higher angles were either too broad or too weak to be useful for accurate measurements. Measurements of the locations of the (002), (040), (400), (001), (020) and (200) peaks were most useful; other resolved peaks in the 20–60° range were measured to check results based on the above. Unit-cell dimensions were computed from these reflection angles without taking account of the fact that the angle β was not exactly 90°; i.e., for these computations the unit cell was treated as though it were orthorhombic. The error introduced by this approximation was less than errors of measurement of individual spacings. The average coefficients of expansion in the ranges 0–300° C. and 300–700° C. are:

Axes	0–300° C.	300–700° C.
<i>a</i>	13 × 10 ⁻⁶	17 × 10 ⁻⁶
<i>b</i>	14	-1.3
<i>c</i>	14	18

It appeared likely that a structural transformation at 300° C. would involve a change from monoclinic to orthorhombic symmetry. That possibility was checked by measurements of the widths of the 221/22 $\bar{1}$, 112/11 $\bar{2}$ and 121/12 $\bar{1}$ reflections, all of which were closely spaced doublets at room temperatures. All three peaks showed essentially the same behavior: from broad peaks (doublets) at room temperature, they showed little change in half widths up to about 260° C.; from 260 to 330° C. the peaks sharpened rapidly, and then did not change detectably in the temperature range studied. The data for the 221/22 $\bar{1}$ are typical; when the diffractometer was run at a speed of $\frac{1}{3}$ ° (2θ) a minute, with a time constant of 8 sec., the half width at room temperature was 0.60–0.65° (2θ). At 180° C. it was 0.55°; at 260° C. it was 0.50° and at 300° C. the half width was close to 0.30° (2θ). Above this temperature no measurable sharpening occurred. As the doublets merged into single peaks near 330° C. the peak intensities increased, in distinction to the behavior of

'normal' reflections, which decreased in intensity with increasing temperature.

It was evident that above 330° C. the unit cell of WO₃ is orthogonal and, in view of the simple atomic arrangement in this structure, probably orthorhombic. The transition from monoclinic to orthorhombic symmetry appears to be a gradual one, extending over at least 100° C., and is characterized primarily by a slow shift of the β angle from 90.9° at room temperature to 90° at 300° C.

The sharp break in the expansion of the *b* axis at about 300° C. was somewhat unexpected in the light of Ueda & Ichinokawa's data; it did agree very well with Foëx's findings. The mean coefficient of linear expansion*, calculated from our X-ray data, is about 13.7 × 10⁻⁶/°C. for the range from 20 to 300° C.; it decreases to about 11.2 × 10⁻⁶/°C. for the range from 300 to 700° C. The very close correspondence between these values and those calculated from Foëx's data (13 × 10⁻⁶ and 10 × 10⁻⁶/°C.) is probably partly coincidental.

The measurements reported by Ueda & Ichinokawa appear to be in error in at least three respects; they indexed their room-temperature powder photographs on the basis of an orthorhombic unit cell; they reported that the *b* axis expanded uniformly over the entire range 0–710° C.; and the values they list for the lengths of both the *a* and *b* axes are too small by 0.2 Å; the last error is probably typographical.

The change in the mean coefficient of expansion of WO₃ at about 300° C. has a counterpart in the expansion coefficients of the cubic sodium tungsten bronzes near that temperature (Rosen, Post & Banks, 1956). The latter show decreases, above their transition temperatures, from 12 × 10⁻⁶/°C. to about 5 × 10⁻⁶/°C. The relation between the behavior of pure WO₃ and WO₃ with sodium in solid solution (the sodium tungsten bronzes) is being studied.

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* As a first approximation the expansion of each of the axes of the unit cell may be considered to be linear over each of the two temperature ranges 20–300° C. and 300–700° C. The 'mean coefficient of linear expansion' is defined as $\alpha = \frac{1}{3}(a_1 + a_2 + a_3)$, where each of the *a*'s has been averaged over the temperature range under consideration; the *a*'s refer to the coefficients of linear expansion in the three axial directions.