

We may now establish the  $y$  co-ordinates of the molecules by reference to the  $a$  projection (Fig. 3(a)). While confirming the conclusion that the molecules are in pairs at  $z = 0$  and  $z = \frac{1}{2}$  (pseudo-origins  $O'$ ), this projection also suggests strongly that they are

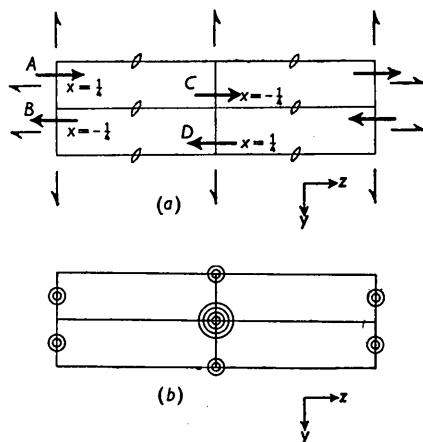


Fig. 5. (a) Arrangement of molecules in the pseudo-orthorhombic unit cell, seen in  $a$  projection. (b) Point-Patterson projection derived from (a).

displaced in neighbouring sheets by  $\frac{1}{4}b$ , giving the pseudo-origins marked  $O''$  at  $y = \frac{1}{4}, z = \frac{1}{2}$ . This arrangement is sketched in Fig. 5(a), which includes all the axes of the pseudo-orthorhombic symmetry; it would yield the point-Patterson shown in Fig. 5(b) which may be compared with Fig. 3(a).

It may thus be concluded that the co-ordinates of the molecules are  $(\frac{1}{4}, \frac{1}{8}, 0)$ ,  $(-\frac{1}{4}, -\frac{3}{8}, 0)$ ,  $(\frac{1}{4}, -\frac{1}{8}, \frac{1}{2})$  and  $(-\frac{1}{4}, \frac{3}{8}, \frac{1}{2})$ , as shown in Figs. 4(b) and 5(a). This unit cell may be sheared slightly to give a monoclinic angle  $\beta = 91^\circ$ ; on the other hand the symmetry of the reflexions is very nearly orthorhombic and it is admittedly very difficult to understand why the structure does not exhibit twinning or disordering as a consequence of its slight distortion from orthorhombic symmetry. The fact is, however, that twinning has not been encountered in this structure.

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## ' $\beta$ -Tungsten' as a Tungsten Oxide

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The existence of ' $\beta$ -W' as a modification of tungsten is contradicted by the low density of the phase and by its decomposition into W and  $WO_2$  at about  $700^\circ C$ . It is assumed that ' $\beta$ -W' is a metallic tungsten oxide with the probable ideal formula  $W_3O$ . The unit cell would then contain  $6W + 2O$  atoms distributed at random over the eight positions of the  $A15$  structure.

### Introduction

The phase, which hitherto has been considered as the  $\beta$  modification of tungsten ( $\beta$ -W), is referred to as the  $A15$  type. The space group is  $Pm\bar{3}n$  with 2 W in (a):  $0, 0, 0$ ;  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ , and 6 W in (c):  $\frac{1}{4}, 0, \frac{1}{2}$ ;  $\frac{1}{2}, \frac{1}{4}, 0$ ;  $0, \frac{1}{2}, \frac{1}{4}$ ;  $\frac{3}{4}, 0, \frac{1}{2}$ ;  $\frac{1}{2}, \frac{3}{4}, 0$ ;  $0, \frac{1}{2}, \frac{3}{4}$ . It has been obtained only by electrolysis of fused mixtures of either tungsten trioxide and alkali metal phosphates (Hartmann, Ebert & Bretschneider, 1931) or of alkali metal tungstates (Burgers & van Liempt, 1931) at temperatures below  $700^\circ C$ . Hartmann *et al.* stated that  $\beta$ -W irreversibly transforms into  $\alpha$ -W at temperatures above  $700^\circ C$ .

### Experimental

The same method of preparation as described by the above mentioned authors was used in the present

investigation, and the reaction temperature was  $625$ – $650^\circ C$ .

Powder photographs were taken in focusing cameras of the Guinier type using  $Cu K\alpha$  radiation. It was found impossible to prepare  $\beta$ -W in a pure state. Some samples contained alkali tungsten bronzes and others  $\alpha$ -W as impurities. One sample of the latter type contained only small amounts of  $\alpha$ -W, and this sample was used in the following study.

### Results and discussion

A lattice constant of  $a = 5.036 \text{ \AA}$  ( $V = 127.7 \text{ \AA}^3$ ) was obtained for  $\beta$ -W, in close agreement with the values given by Hartmann *et al.* (1931) and Neuburger (1933). The  $p|F|^2$  values calculated for the  $A15$  arrangement of atoms were further in good agreement with

those given by the former authors and with the observed relative intensities. Hartmann *et al.* obtained a density of  $12.30 \pm 0.25$  g.cm.<sup>-3</sup> for a pure sample of  $\beta$ -W, i.e. 35% lower than the value 19.1 g.cm.<sup>-3</sup> calculated for eight metal atoms in the unit cell. The said authors assumed the great discrepancy to be due to extremely small crystals. For the sample used in the present study a density of 15.0 g.cm.<sup>-3</sup> was obtained, which is 20% too low. It is most unlikely, however, that such a low value could depend upon the size of the crystals. For pure  $\alpha$ -W (Söderfors, 99.9%, grain size  $\sim 1\mu$ ) with a cubical axial length of  $a = 3.156$  Å ( $V = 31.49$  Å<sup>3</sup>) the calculated density is 19.4 g.cm.<sup>-3</sup>. The observed value was 18.5 g.cm.<sup>-3</sup>, corresponding to an error of 5% as compared with the calculated value. Assuming that the accuracy of the density determination of  $\beta$ -W is of the same order, and noticing that the  $\beta$ -W sample contained a small amount of  $\alpha$ -W, the density observed for  $\beta$ -W corresponds to a cell content of six metal atoms instead of eight, i.e. a calculated value of 14.4 g.cm.<sup>-3</sup> instead of 19.1 g.cm.<sup>-3</sup>. From  $p|F|^2$  calculations it is evident that the metal atoms are then distributed at random over the eight atomic positions (a)+(c) in the A15 unit cell.

As was said above, Hartmann *et al.* stated that  $\beta$ -W irreversibly transforms into  $\alpha$ -W at temperatures above 700°C. In the present investigation a sample heated at 700°C. for two days in an evacuated and sealed silica tube still contained small amounts of  $\beta$ -W while all  $\beta$ -W had disappeared in a sample heated at 750°C. for three hours. But at the same time tungsten dioxide had been formed, as indicated by the presence of comparatively weak diffraction lines of WO<sub>2</sub> in the powder photographs. Samples of pure  $\alpha$ -W (99.9%) did not show any traces of WO<sub>2</sub> after heating under the same conditions. This excludes the possibility that the formation of WO<sub>2</sub> in the former samples was caused by a reaction with the silica tube.

It is here assumed that ' $\beta$ -W' is a metallic oxide and that in all probability it cannot exist in an oxygen-free state. The oxygen content could not be determined but a consideration of the available space gives a probable maximum value.

One can assume that the distance between tungsten and oxygen atoms certainly cannot be less than 1.8 Å. If the six tungsten atoms are distributed at random over the eight (a)+(c) positions of the A15 cell the only possible places for oxygen atoms will then be the two remaining (a)+(c) positions. If both are filled the cell will contain 6 W + 2 O distributed at random over (a)+(c), i.e. the oxide could be written W<sub>3</sub>O. The density calculated for an oxide with 2 W<sub>3</sub>O per cell is 14.8 g.cm.<sup>-3</sup>, in good agreement with the observed value of 15.0 g.cm.<sup>-3</sup> for the sample of ' $\beta$ -W' containing a small amount of  $\alpha$ -W. At about 700°C. an oxide

W<sub>3</sub>O would decompose according to the reaction formula:  $2 W_3O = 5 W + WO_2$ .

An analogous metallic oxide has recently been found to exist in the Cr-O system by one of the present authors (Schönberg, 1954). This phase has the ideal formula Cr<sub>3</sub>O. It also belongs to the space group *Pm3n* but in this case the atoms occupy ordered positions, namely 2 O in 2(a) and 6 Cr in 6(c). Cr<sub>3</sub>O is isomorphous with V<sub>3</sub>Si (Wallbaum, 1939), Cr<sub>3</sub>Si (Borén, 1933), Mo<sub>3</sub>Si (Templeton & Dauben, 1950), V<sub>3</sub>Ge and Cr<sub>3</sub>Ge (Wallbaum, 1944). This adds support to the assumption that the formula of ' $\beta$ -W' is W<sub>3</sub>O.

The fact that the atoms of the new oxide are distributed with a very high degree of randomness over the positions (a)+(c) is clearly shown by the powder photographs. Considering the large scattering factor of the tungsten atoms, the fact that reflexions with  $h = 2n+1$ ,  $k = 2n+1$ ,  $l = 4n$  and  $h = 4n+2$ ,  $k = 4n+2$ ,  $l = 4n$  ( $h, k, l$  permutable) are absent is not compatible with an ordered distribution.

Attempts to prepare ' $\beta$ -W' by careful oxidation of tungsten powder at temperatures below 700°C. have failed owing to the ease with which the trioxide WO<sub>3</sub> forms. Another method, which we have not yet tried, would be an almost complete reduction of one of the higher oxides with a reducing gas.

We have also tried to prepare a molybdenum oxide, analogous with Cr<sub>3</sub>O and ' $\beta$ -W'. The same method as was used for the preparation of ' $\beta$ -W' failed, but heating of mixtures of Mo powder and MoO<sub>2</sub> at a comparatively low temperature gave an oxide with the probable formula Mo<sub>3</sub>O. It has an anti-BiF<sub>3</sub> structure where only three-quarters of the positions are occupied by atoms (Schönberg, 1954).

The compound Mo<sub>3</sub>Zr of the A15 type, reported by Wallbaum (1942), is probably an oxide (Mo,Zr)<sub>3</sub>O, as an investigation, undertaken by the present authors, shows that the only intermediate phase existing in the Mo-Zr system is Mo<sub>3</sub>Zr of the Laves C15 type.

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