Fig. 1. Projection de la structure le long de c.

Chaque atome de cadmium est pentacoordonné, il est au centre d'une bipyramide déformée constituée par trois atomes d'arsenic et par deux atomes d'iode. Les liaisons varient de 2,62 à 2,74 Å pour Cd—As et de 2,98 à 3,43 Å pour Cd—I, elles sont comparables respectivement aux liaisons observées dans $CdAs_2$ (2,69 Å; Horn & Lukaszewicz, 1968) et CdI_2 (2,99 Å; Wyckoff, 1963).

Chaque atome d'iode est entouré par quatre atomes de cadmium, l'ensemble étant sensiblement coplanaire. Dans les files Cd—I—Cd—I... les angles I—Cd—I valent 167 et 170°.

Il n'y a aucune liaison Cd—Cd ni aucune liaison As—I, les plus courtes distances Cd—Cd et As—I étant respectivement de 3,90 et 3,88 Å. Formellement, le polyanion a une charge n fois négative. Si l'on applique la formule classique des composés de valence (Parthé, 1972) on trouve que le nombre de liaisons anion—anion par anion est de 1,5 ce qui correspond bien à deux liaisons anion—anion par arsenic, l'iode ne participant pas à ces liaisons polyanioniques.

Discussion. Cette structure est caractérisée par la présence d'une hélice d'atomes d'arsenic parallèle à l'axe c. La liaison As—As, la plus courte de la structure, est sensiblement constante (2,42 à 2,43 Å) et comparable à celles observées dans d'autres combinaisons polyanioniques de l'arsenic: 2,43 Å dans $CdAs_2$ (Horn & Lukaszewicz, 1968) et 2,40 Å dans $Cd_4As_2I_3$ (Gallay, 1975). Ces différentes hélices sont reliées entre elles par les atomes de cadmium.

Chaque atome d'arsenic est entouré par les deux atomes d'arsenic de l'hélice et par deux atomes de cadmium, ces quatre voisins constituant un tétraèdre très déformé.

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Tungsten Dioxide: Structure Refinement by Powder Neutron Diffraction

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Abstract. WO_2, monoclinic, space group $P2_1/c$, $a = 5.563$ (2), $b = 4.896$ (3), $c = 5.663$ (2) Å, $\beta = 120.47$ (1)° (298 K). The structure has been refined by profile analysis of powder neutron diffraction data at room temperature. It is a monoclinically distorted rutile structure with alternate W—W lengths of 2·475 and 3·096 Å along the rutile chains.

Introduction. WO_2 exists as a line phase at ambient pressures over the temperature range $273 < T < 1803$ K (Phase Diagrams for Ceramists, 1969). Powder X-ray data show that it is isostructural with MoO_2 (Magnéli & Andersson, 1955).

WO_2 was prepared by reduction of WO_3 (Koch Light Laboratories) in a static H_2/H_2O atmosphere,

with H_2/H_2O pressure ratio of 7·7:1, at 1023 K for 24 h. The product, a brown powder, was characterized by its powder X-ray pattern and the composition $WO_{2.00(1)}$ confirmed by its reducing power (Chaoin & Marion, 1963) and by thermogravimetric reduction.

The neutron powder profile was recorded on the diffractometer PANDA at AERE Harwell in the 2θ range 10 to 110° in steps of 0·1°. The sample (~10 g) was contained in a thin-walled vanadium can. The powder profile was recorded at room temperature with a neutron wavelength of 1·2615 Å, obtained by reflexion from the (511) planes of a Ge monochromator with a take-off angle of 70°.

MoO_2 has been the subject of a single-crystal X-ray investigation (Brandt & Skapski, 1967). The space group is $P2_1/c$ with specific absences 0k0, $k = 2n + 1$ and h0l, $l = 2n + 1$. Both powder X-ray and powder neutron profiles for WO_2 may be indexed on this scheme, there being no evidence for the space group $P2_1$. Thus the method of least-squares profile refinement (Rietveld, 1969) was applied in the space group $P2_1/c$, with as starting parameters the atomic coordinates of MoO_2. This program minimizes the function $\chi^2 = \sum_i w_i[y_i(\text{obs}) - cy_i(\text{calc})]^2$, where w_i is the weighting function, y_i is the number of counts at the point $2\theta_i$ and c is the scale factor. The scattering lengths were $b_W = 0\cdot48$, $b_O = 0\cdot580 \times 10^{-14}$ m (Bacon, 1972). The refinement included the scale factor, three halfwidth parameters, the zero-point correction, the lattice constants, nine positional parameters, three thermal parameters and the peak asymmetry parameter for peaks below $2\theta = 40°$.

$$R_{\text{profile}} = 100 \left\{ \frac{\sum_i w_i[y_i(\text{obs}) - cy_i(\text{calc})]^2}{\sum_i w_i[y_i(\text{obs})]^2} \right\}^{1/2}$$

converged to 9·28 compared with 9·35 expected on purely statistical grounds. $R_I = 100 \sum |I_{\text{obs}} - cI_{\text{calc}}|/\sum I_{\text{obs}}$ was 6·08. Atom parameters are given in Table 1, and the agreement between observed and calculated profiles is shown in Fig. 1.

Discussion. Bond angles and distances are given in Table 2. A projection of the structure on (010) is given in Fig. 2. The bond lengths are derived from the X-ray lattice parameters.

The structural details of WO_2 and MoO_2 are very similar, both being of a monoclinically distorted rutile

Table 1. *Atom parameters for* WO_2

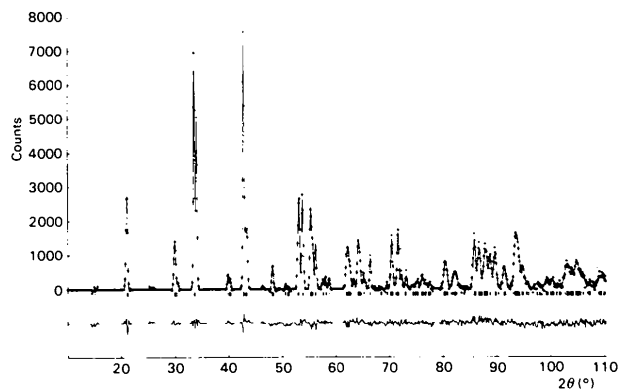|	x	y	z	B (Å²)
W	0·2278 (11)	−0·0102 (14)	0·0111 (12)	0·19 (5)
O(1)	0·1119 (11)	0·2186 (11)	0·2334 (8)	0·31 (7)
O(2)	0·3900 (9)	0·7024 (12)	0·2986 (9)	0·57 (8)

Fig. 1. Observed and calculated profiles for WO_2: ● observed; — calculated. Upper trace: reflexions; lower trace: difference plot.

Table 2. *Interatomic distances and angles in* WO_2

(a) Interatomic distances (Å) (primed symbols represent atoms on an adjacent plane)

W(1)—W(2)	2·475 (2)	O1(1)—O1(4)	2·796 (2)
W(1)—W(3)	3·096 (2)	O1(1)—O2(1)'	2·750 (2)
		O1(2)—O2(3)'	2·706 (1)
		O1(1)—O2(4)	2·721 (1)
		O1(1)—O2(5)'	3·445 (1)
		O2(1)—O2(4)	2·792 (1)
Within WO_6 octahedron			
W(1)—O1(1)	2·019 (2)	O1(1)—O1(2)	2·848 (1)
W(1)—O1(2)	1·975 (2)	O1(1)—O2(3)	2·868 (2)
W(1)—O1(3)	1·969 (1)	O1(1)—O1(3)	3·128 (1)
W(1)—O2(1)	1·989 (2)	O1(1)—O2(1)	2·887 (2)
W(1)—O2(2)	2·061 (2)	O2(1)—O2(3)	2·912 (2)
W(1)—O2(3)	2·107 (1)	O2(1)—O2(2)	2·870 (2)

(b) Bond angles (°) (typical e.s.d. for angles = 0·1°)

W(2)—W(1)—W(3)   173·9

Within WO_6 octahedron

Around W		Around O(1)	
O1(1)—W(1)—O2(2)	171·8	O1(2)—O1(1)—O2(3)	56·9
O1(2)—W(1)—O2(1)	173·2	O2(3)—O1(1)—O2(1)	60·8
O1(3)—W(1)—O2(3)	167·2	O2(1)—O1(1)—O1(3)	57·8
O1(1)—W(1)—O1(3)	103·3	O1(2)—O1(1)—O2(1)	87·2
O1(1)—W(1)—O1(2)	91·0		
O1(1)—W(1)—O2(1)	92·2	Around O(2)	
O1(1)—W(1)—O2(3)	88·0	O1(1)—O2(1)—O2(3)	59·3
O2(1)—W(1)—O1(3)	94·8	O2(2)—O2(1)—O2(3)	57·8
O2(1)—W(1)—O2(3)	90·6	O2(2)—O2(1)—O1(3)	55·8
O2(1)—W(1)—O2(2)	90·2	O2(2)—O2(1)—O1(1)	90·0
O2(3)—W(1)—O2(2)	84·1		
O2(3)—W(1)—O1(2)	83·5		

type, with the bond lengths in the WO_6 octahedra slightly longer (average W—O = 2·020, average Mo—O = 2·011 Å). This is consistent with the ionic radii of W^{4+} and Mo^{4+} (0·66 and 0·650 Å, respectively, Shannon, 1976). The important structural feature is the occurrence of alternately short and long W—W distances down the rutile chains (the a axis). This has been rationalized in terms of metal–metal bonds (Sleight, Hare & Sleight, 1968) and is also seen in other metal dioxides with rutile-related structures
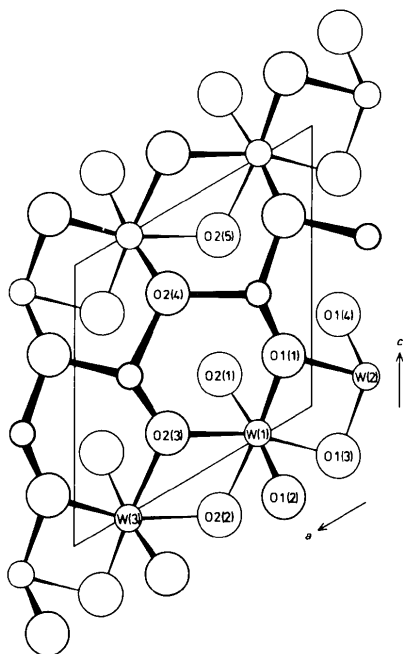
Fig. 2. A projection of the structure of WO_2 on to the (010) plane.

such as VO_2, TcO_2 and NbO_2 (Rogers, Shannon, Sleight & Gillson, 1969) as well as in $AlWO_4$ (Doumerc, Vlasse, Pouchard & Hagenmuller, 1975) and $GaWO_4$ (Palmer, 1977).

There is no evidence for the space group $P2_1$ as suggested by Magnéli & Andersson (1955) from either the X-ray or neutron powder profiles: the symmetry

and size of the unit cell of WO_2 are such that there would be no fully resolved peaks $h0l$, $l = 2n + 1$ in the 2θ range investigated. However, refinement was attempted in $P2_1$; no improvement in the agreement between observed and calculated profiles was seen, and indeed the atomic coordinates refined effectively to the symmetry-equivalent positions in $P2_1/c$.

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Dieuropium(III) Germanate Oxide

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Abstract. $Eu_2(GeO_4)O$, monoclinic, $P2_1/c$, $a = 9.977$ (7), $b = 7.136$ (4), $c = 6.854$ (4) Å, $\beta = 115.78$ (6)°, $Z = 8$, $D_m = 6.84$ (2), $D_x = 6.90$ Mg m^{-3}. Crystals were prepared by melting a pre-sintered mixture of Eu_2O_3 and GeO_2 in an image furnace with a tungsten halogen lamp as heat source. The seven-coordination polyhedra of Eu^{3+} ions in a set of equivalent sites form slabs parallel to (100) by edge-sharing. These slabs are connected to the corrugated layers of the edge-shared polyhedra of seven-coordinated Eu^{3+} ions in other equivalent positions through common edges of the polyhedra and O—Ge—O bonds of the GeO_4 tetrahedra.

Introduction. Of the germanates and silicates of the rare-earth elements Ln_2XO_5 (Ln = Sc, Y, La, Ce, ...,

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