

The Crystal Structures of  $\text{Mo}_2\text{As}_3$  and  $\text{W}_2\text{As}_3$ 

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The compounds  $\text{Mo}_2\text{As}_3$  and  $\text{W}_2\text{As}_3$  are isostructural. The monoclinic unit cells have the dimensions:

$\text{Mo}_2\text{As}_3$ :  $a = 16.061 \pm 0.002 \text{ \AA}$ ,  $b = 3.2349 \pm 0.0004 \text{ \AA}$ ,

$c = 9.643 \pm 0.001 \text{ \AA}$ ,  $\beta = 136.74 \pm 0.02^\circ$

$\text{W}_2\text{As}_3$ :  $a = 15.966 \pm 0.001 \text{ \AA}$ ,  $b = 3.2791 \pm 0.0004 \text{ \AA}$ ,

$c = 9.599 \pm 0.001 \text{ \AA}$ ,  $\beta = 136.648 \pm 0.006^\circ$

The space group is  $C2/m$  and the unit cell contains  $2 \times 4$  Mo (W) and  $3 \times 4$  As in positions 4 (*i*). The values of  $x$ ,  $z$ , and  $B$  ( $\text{\AA}^2$ ) were found to be

$\text{Mo}_I$ :  $x_1 = 0.2482 \pm 0.0009$ ,  $z_1 = 0.1252 \pm 0.0015$ ,  $B_1 = 1.1 \pm 0.2$ ;  $\text{Mo}_{II}$ :

$x_2 = 0.3511 \pm 0.0009$ ,  $z_2 = 0.5667 \pm 0.0015$ ,  $B_2 = 1.2 \pm 0.2$ ;  $\text{As}_I$ :  $x_3 =$

$0.1270 \pm 0.0012$ ,  $z_3 = 0.2069 \pm 0.0020$ ,  $B_3 = 1.3 \pm 0.3$ ;  $\text{As}_{II}$ :  $x_4 =$

$0.4145 \pm 0.0013$ ,  $z_4 = 0.1435 \pm 0.0021$ ,  $B_4 = 1.4 \pm 0.3$ ;  $\text{As}_{III}$ :  $x_5 =$

$0.1035 \pm 0.0012$ ,  $z_5 = 0.5795 \pm 0.0020$ ,  $B_5 = 1.2 \pm 0.3$  for  $\text{Mo}_2\text{As}_3$  and

$\text{W}_I$ :  $x_1 = 0.2520 \pm 0.0012$ ,  $z_1 = 0.1243 \pm 0.0020$ ,  $B_1 = 2.2 \pm 0.4$ ;  $\text{W}_{II}$ :

$x_2 = 0.3485 \pm 0.0012$ ,  $z_2 = 0.5672 \pm 0.0020$ ,  $B_2 = 2.1 \pm 0.4$ ;  $\text{As}_I$ :  $x_3 =$

$0.1249 \pm 0.0027$ ,  $z_3 = 0.2033 \pm 0.0048$ ,  $B_3 = 1.7 \pm 0.7$ ;  $\text{As}_{II}$ :  $x_4 =$

$0.4168 \pm 0.0029$ ,  $z_4 = 0.1457 \pm 0.0051$ ,  $B_4 = 1.8 \pm 0.7$ ;  $\text{As}_{III}$ :  $x_5 =$

$0.1051 \pm 0.0027$ ,  $z_5 = 0.5796 \pm 0.0050$ ,  $B_5 = 1.6 \pm 0.7$  for  $\text{W}_2\text{As}_3$ .

The  $\text{Mo}_2\text{As}_3$  ( $\text{W}_2\text{As}_3$ ) structure is discussed in relation to the general (8-N) rule.

The existence of the compounds  $\text{Mo}_2\text{As}_3$  and  $\text{W}_2\text{As}_3$  has recently been established as a result of independent studies of the systems molybdenum — arsenic and tungsten — arsenic by Boller and Nowotny,<sup>1</sup> Taylor *et al.*,<sup>2</sup> and Jensen *et al.*,<sup>3,4</sup> However, with respect to the compositions of these compounds the three studies conclude somewhat differently. Boller and Nowotny<sup>1</sup> arrived at the incorrect composition  $T_4\text{As}_5$ ,\* whereas Taylor *et al.*<sup>2</sup> report that they were unable to exclude completely the formulae  $T_8\text{As}_{11}$  and  $T_8\text{As}_{13}$  although they consider  $T_2\text{As}_3$  to be the most probable composition. Jensen *et al.*<sup>3,4</sup> were, on the other hand, able to give unambiguous evidence for the formula  $T_2\text{As}_3$  by means of different experimental methods, and showed furthermore that no extended ranges of homogeneity of these phases exist.

Two further independent studies of the same systems have recently been carried out by Hulliger<sup>5</sup> and Brown.<sup>6</sup> The latter papers<sup>5,6</sup> are concerned only

\* The symbol *T* is throughout this paper being used as a common notation for Mo and W.

with the arsenic rich phases, containing  $\geq 66.67$  atomic % As, and the existence of the  $T_2As_3$  compounds is accordingly not mentioned.

The present paper describes the determination of the crystal structures of these compounds. (A brief description of the results has been given in a previous communication.<sup>3</sup>) The atomic arrangement in these structures is of considerable interest as a source for information on the chemical bonding, especially in relation to the application of the general (8-N) rule.

## RESULTS

(i) *Unit cell and space group.* According to Jensen *et al.*<sup>3,4</sup>  $T_2As_3$  crystallizes monoclinically with the unit cell dimensions:

$$\begin{aligned} Mo_2As_3: & a = 16.061 \pm 0.002 \text{ \AA}, b = 3.2349 \pm 0.0004 \text{ \AA}, \\ & c = 9.643 \pm 0.001 \text{ \AA}, \beta = 136.74 \pm 0.02^\circ \\ W_2As_3: & a = 15.966 \pm 0.001 \text{ \AA}, b = 3.2791 \pm 0.0004 \text{ \AA}, \\ & c = 9.599 \pm 0.001 \text{ \AA}, \beta = 136.648 \pm 0.006^\circ \end{aligned}$$

The lattice dimensions are calculated from Guinier photograph data (taken with strictly monochromatized  $CuK\alpha_1$  radiation,  $\lambda = 1.54050 \text{ \AA}$ , using KCl as internal standard) by applying the method of least squares. The indicated error limits correspond to twice the standard deviations obtained in these calculation.

Taylor *et al.*<sup>2</sup> have chosen a somewhat different unit cell for  $T_2As_3$ . The transformation matrix for axes and indices from the cell chosen by Taylor *et al.* to that used in the present paper and *vice versa* is 102/010/001 and the differences concern accordingly only the  $a$ -axes and the  $\beta$ -angles. Numerical data for comparison of the size of the unit cell of  $T_2As_3$ , as determined by Boller and Nowotny<sup>1</sup> (their choice of unit cell represents only a pseudo cell), Taylor *et al.*,<sup>2</sup> and Jensen *et al.*,<sup>3,4</sup> are tabulated by Jensen *et al.*<sup>4</sup> The shape of the unit cell proposed by Taylor *et al.* corresponds to a shorter  $a$ -axis and a more nearly right-angled value for  $\beta$  compared with that used in the present paper. On transforming the present axes for  $T_2As_3$  using the matrix 101/010/001 the unit cell assumes an even smaller  $a$ -value and a  $\beta$ -value nearer  $90^\circ$ . (The lattice dimensions for this setting of the unit cell are:  $a = 11.197 \pm 0.002 \text{ \AA}$ ,  $b = 3.2349 \pm 0.0004 \text{ \AA}$ ,  $c = 9.643 \pm 0.001 \text{ \AA}$ ,  $\beta = 100.57 \pm 0.02^\circ$  for  $Mo_2As_3$  and  $a = 11.143 \pm 0.001 \text{ \AA}$ ,  $b = 3.2791 \pm 0.0004 \text{ \AA}$ ,  $c = 9.599 \pm 0.001 \text{ \AA}$ ,  $\beta = 100.40 \pm 0.006^\circ$  for  $W_2As_3$ .) Although the three choices of unit cell are equivalent (having the equal volume and leading to the same possible space groups), the latter setting of the unit cell is more conventional. In an attempt to avoid confusion we have nevertheless decided to adopt the same setting of the unit cell as used in our previous communications.<sup>3,4</sup>

The observed densities at  $25.00^\circ C$ ,  $8.07 \text{ g cm}^{-3}$  ( $Mo_2As_3$ ) and  $11.32 \text{ g cm}^{-3}$  ( $W_2As_3$ ), show that the unit cell contains 4  $T_2As_3$ -groups ( $Z_c = 4.00$  for  $Mo_2As_3$  and  $Z_c = 3.97$  for  $W_2As_3$ ).

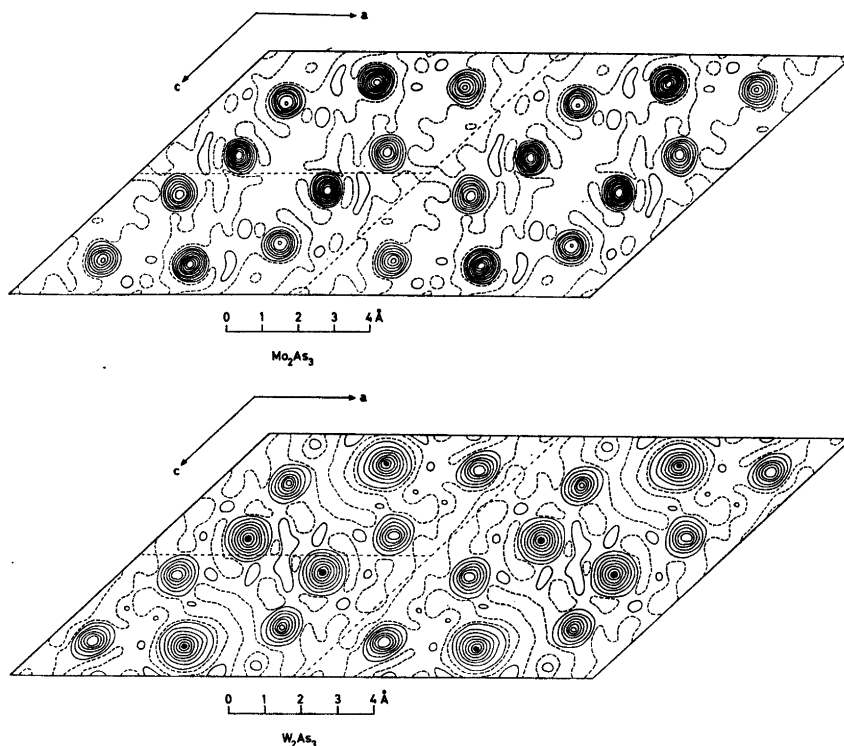
A large number of  $T_2As_3$  single crystals was obtained by means of chemical transport reactions using traces of chlorine, bromine, or iodine as a transport agent. The crystals were of needle shape with the diad axis along the needle axis.

All reflections of the type  $hkl$  with  $h + k = 2n + 1$  are missing in the X-ray photographs and the possible space groups are accordingly  $C2$ ,  $Cm$ , and  $C2/m$ .

(ii) *(010)-Projection.* Intensity measurements of the  $h0l$  and  $h1l$  reflections

were carried out microphotometrically using the multiple-film technique. (The X-ray photographs were obtained in an integrating Weissenberg camera of 57.3 mm diameter with  $\text{CuK}\alpha$ -radiation.) The intensities were corrected for the combined Lorentz and polarization factor and for absorption ( $\mu R = 1.5$  for  $\text{Mo}_2\text{As}_3$  and  $\mu R = 2.5$  for  $\text{W}_2\text{As}_3$ ). For the calculation of  $F_c$ -values the atomic scattering factors were taken from *International Tables*.<sup>7</sup> The agreement between  $F_o$  and  $F_c$  is expressed by the reliability index  $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ . (Undetected reflections are not included in these calculations.)

Because of the short  $b$ -axes, it was decided to start with Patterson syntheses on the basis of the corrected  $F_o^2(h0l)$ -values. The two space groups  $C2$  and  $C2/m$  can be distinguished from the space group  $Cm$  by the presence or absence of a centre of symmetry in the  $(010)$ -projection. (The short  $b$ -axes exclude the general position  $4(b)$  of  $Cm$  which would lead to interatomic distances  $\leq 1.6$  Å. All the atoms may nevertheless occupy the special position  $2(a)$ .) Statistical  $N(z)$  tests<sup>8</sup> were therefore applied to the intensities of the  $h0l$  reflections. The  $N(z)$  versus  $z$  distributions suggested non-centrosymmetric projections, *i.e.* the space group  $Cm$ , for both compounds. This knowledge was accordingly taken into consideration in the first attempts to derive trial structures from examina-



*Fig. 1.* Electron density projections of  $\text{Mo}_2\text{As}_3$  and  $\text{W}_2\text{As}_3$  along  $[010]$ . Contours are at intervals of  $10 \text{ e}\text{\AA}^{-2}$  generally, and at  $20 \text{ e}\text{\AA}^{-2}$  around the tungsten atoms, which have filled centres. The zero contours are broken.

Table 1. Observed and calculated structure factors for  $\text{Mo}_2\text{As}_3$  and  $\text{W}_2\text{As}_3$ . (The three numbers in each column represent respectively  $h$ ,  $10F_o$ , and  $10F_c$ .)

$\text{Mo}_2\text{As}_3$			$\text{Mo}_2\text{As}_3$			$\text{Mo}_2\text{As}_3$			$\text{Mo}_2\text{As}_3$		
$k = 0, l = -12$			$k = 0, l = -6$			6 2450 -2450			$k = 0, l = 7$		
12	553	-619	2	906	843	8	1264	-1321	0	1313	1433
14	719	669	4	1714	1743	10	829	806	2	489	-560
16	453	-431	6	1102	-1133	12	0	-207	$k = 0, l = 8$		
$k = 0, l = -11$			$k = 0, l = -5$			14 903 -883			0 0 -195		
8	1069	-1164	2	1793	1777	$k = 0, l = 0$			$k = 1, l = -11$		
10	0	175	4	2526	-2574	2	1472	-1144	11	0	-22
12	0	54	6	421	422	4	2310	-2194	13	303	304
14	0	251	8	1165	1273	6	1570	-1597	15	0	-120
16	604	-544	10	0	77	8	1944	1925	17	0	-102
18	1185	1073	12	2127	-2193	10	670	-667	$k = 1, l = -10$		
$k = 0, l = -10$			$k = 0, l = -4$			12 781 722			7 277 -252		
6	0	-49	2	0	-36	$k = 0, l = 1$			9 554 529		
8	1239	1371	4	825	757	0	442	-316	11 548 -536		
10	464	457	6	2729	3247	2	1028	-912	13 746 663		
12	1872	-1942	8	2474	-2818	4	3065	2972	15 830 -703		
14	557	-540	10	564	-489	6	782	-726	17 844 -769		
16	1314	1222	12	0	-203	8	872	-872	$k = 1, l = -9$		
18	651	592	14	1193	1197	10	803	-852	3 375 354		
20	563	-564	16	720	-638	12	820	858	5 0 122		
$k = 0, l = -9$			$k = 0, l = -3$			$k = 0, l = 2$			7 1160 -1190		
2	782	-944	2	312	-217	0	504	343	9 513 491		
4	0	-170	4	902	-941	2	249	206	11 570 -576		
6	0	328	6	1830	2199	4	0	-241	13 1179 719		
8	592	630	8	654	698	6	534	478	15 446 365		
10	963	-924	10	0	326	8	380	348	17 442 346		
12	1011	982	12	2054	-2101	10	745	-739	19 1567 -1449		
14	0	-137	14	541	497	$k = 0, l = 3$			$k = 1, l = -8$		
16	780	-684	16	0	125	0	3163	-2779	1 466 -538		
18	687	-603	$k = 0, l = -2$			2	1184	1114	3 489 -519		
20	1165	1041	2	811	-718	4	1496	1426	5 1276 1403		
$k = 0, l = -8$			4	0	-135	6	495	443	7 1036 1072		
2	1105	-1200	6	0	126	8	1414	-1582	9 1539 -1586		
4	1000	1028	8	803	-848	$k = 0, l = 4$			11 1418 -1457		
6	693	-711	10	778	770	0	1914	-1779	13 1253 1191		
8	781	779	12	1238	1218	2	1168	1124	15 717 632		
10	0	-358	14	620	-586	4	1315	-1346	17 0 -191		
12	643	634	16	1267	-1300	6	596	618	19 0 3		
14	1034	-941	$k = 0, l = -1$			8	511	570	$k = 1, l = -7$		
16	1017	869	2	275	-219	$k = 0, l = 5$			1 950 -1007		
18	958	-794	4	810	829	0	912	827	3 1522 1559		
$k = 0, l = -7$			$k = 0, l = -1$			2	382	-372	5 0 -165		
2	0	120	2	275	-219	4	1188	-1296	7 710 -663		
4	0	-279	4	810	829	6	578	666	9 0 -98		
6	1544	-1571	$k = 0, l = 6$			$k = 0, l = 6$			11 1579 1649		
8	362	415	0	709	-739	0	709	-739	13 1425 1411		
10	0	-193	2	0	-287	2	0	-287	15 734 -648		
12	2076	2062	4	0	84	4	0	84	17 539 393		
14	519	-445	$k = 0, l = 6$			$k = 0, l = 6$			19 1060 970		
16	1035	-939	0	709	-739	$k = 0, l = 6$					
18	984	-815	2	0	-287	$k = 0, l = 6$					
			4	0	84	$k = 0, l = 6$					

$k = 1, l = -6$	11 0 - 272	5 1866 2148	9 373 - 367
1 561 - 522	13 700 652	7 0 196	
3 673 617	15 977 859	9 0 - 361	$k = 1, l = 3$
5 1135 - 1162	17 1207 - 1063	11 1418 - 1453	1 1173 1066
7 1868 2044		13 764 678	3 1662 1636
9 534 - 503	$k = 1, l = -3$		5 1720 - 1802
11 0 - 144	1 501 - 449	$k = 1, l = 0$	7 300 277
13 1032 - 996	3 1934 - 1981	1 170 - 123	9 0 - 47
15 1084 980	5 1953 2429	3 0 119	
17 792 - 635	7 677 - 743	5 532 - 533	$k = 1, l = 4$
	9 962 - 999	7 0 13	1 0 40
$k = 1, l = -5$	11 0 - 67	9 1275 1257	3 0 - 313
1 1026 - 969	13 1425 1413	11 0 - 147	5 0 106
3 913 - 833	15 733 - 661	13 1002 - 1020	7 0 - 105
5 1456 - 1513			
7 1125 1190	$k = 1, l = -2$	$k = 1, l = 1$	$k = 1, l = 5$
9 747 782	1 3060 2912	1 1781 - 1610	1 1975 2025
11 1458 1504	3 2017 2347	3 864 - 765	3 0 188
13 1928 - 1897	5 0 132	5 0 71	5 467 - 487
15 550 - 437	7 2867 - 3716	7 2001 2170	7 0 - 551
17 289 233	9 1109 1190	9 902 - 954	
	11 0 178	11 622 - 615	$k = 1, l = 6$
$k = 1, l = -4$	13 645 635		1 0 - 134
1 1233 1182	15 496 - 503	$k = 1, l = 2$	3 891 - 923
3 0 - 61		1 3545 - 3507	
5 1337 - 1462	$k = 1, l = -1$	3 0 129	$k = 1, l = 7$
7 0 174	1 1118 1014	5 356 - 288	1 292 - 274
9 0 211	3 907 - 1115	7 531 533	3 0 35

 $\text{W}_2\text{As}_3$ 

$k = 0, l = -10$	$k = 0, l = -7$	12 2488 - 2782	6 1079 1108
6 0 - 213	2 0 - 279	14 1743 1719	8 1522 - 1521
8 1507 1560	4 0 - 443	16 0 275	10 622 605
10 0 402	6 1332 - 1425	18 0 93	12 1579 1679
12 1784 - 2262	8 1096 1082	$k = 0, l = -4$	14 662 - 614
14 0 - 147	10 1303 - 1314	2 0 79	16 1639 - 1483
16 1489 1310	12 2453 2668	4 677 581	
	14 0 - 439	6 4067 4428	$k = 0, l = -1$
$k = 0, l = -9$	16 976 - 962	8 3976 - 4505	2 0 - 151
2 850 - 1265	18 1127 - 898	10 717 679	4 2153 2062
4 0 74		12 490 - 332	6 4031 - 4060
6 435 507	$k = 0, l = -6$	14 1045 931	8 1788 1851
8 579 549	2 741 682	16 1028 - 903	10 1012 902
10 1631 - 1397	4 2066 2311		12 0 - 262
12 1769 1704	6 1399 - 1564	$k = 0, l = -3$	14 1072 - 871
14 0 - 487	8 1999 - 2166	2 1736 1636	
16 898 - 866	10 1172 1129	4 2359 - 2175	$k = 0, l = 0$
	12 920 864	6 2293 2249	2 3355 - 2747
$k = 1, l = -8$	14 933 - 902	8 863 889	4 2265 - 1880
2 1063 - 1184	16 1018 994	10 825 850	6 1834 - 1618
4 1525 1625	18 0 178	12 2702 - 2980	8 2538 2484
6 1491 - 1642	$k = 0, l = -5$	14 1280 1131	10 1796 - 1582
8 1225 1309	2 2476 2650	16 0 19	12 1642 1155
10 0 - 356	4 3890 - 3925		14 0 - 260
12 709 669	6 1418 1156	$k = 0, l = -2$	
14 1500 - 1371	8 2092 1527	2 2448 - 1805	$k = 0, l = 1$
16 1721 1612	10 0 - 146	4 0 - 201	0 897 - 555
18 1415 - 1276			2 1554 - 1721



tions of the Patterson syntheses, the sharpened Patterson syntheses, and the  $\text{W}_2\text{As}_3$ – $\text{Mo}_2\text{As}_3$  difference Patterson synthesis. The limitation to the space group  $Cm$  was, however, removed at a later stage as the  $N(z)$  tests only have supervisory value in these cases where the apparent lack of centre of symmetry may reflect the effects of, *e.g.*, secondary extinction. Some 50 structure proposals (with or without centre of symmetry) were tried, but all endeavours were unsuccessful.

Direct methods for sign determination were then attempted (assuming centrosymmetric projections). The intensities were converted to unitary structure factors and application of Harker-Kasper inequalities<sup>9–11</sup> gave signs (8 probable combinations) for 54 (51) out of 108 (104) structure factors for  $\text{Mo}_2\text{As}_3$  ( $\text{W}_2\text{As}_3$ ). Structure factors calculated on the basis of the atomic parameters deduced from the Fourier syntheses corresponding to the fourth set of signs tried, gave  $R = 0.26$  for  $\text{Mo}_2\text{As}_3$  and  $R = 0.28$  for  $\text{W}_2\text{As}_3$ .  $R$  was improved to 0.18 (0.20) after one (two) further Fourier synthesis for  $\text{Mo}_2\text{As}_3$  ( $\text{W}_2\text{As}_3$ ) and the final Fourier maps (Fig. 1) showed all atoms well resolved. Further improvement of the atomic parameters was obtained by least-square refinements. These refinements were terminated with  $R = 0.073$  for  $\text{Mo}_2\text{As}_3$  and  $R = 0.094$  for  $\text{W}_2\text{As}_3$  after six cycles. (Three cycles were carried out before and three after correction for secondary extinction<sup>12</sup> for both compounds.) The observed and calculated structure factors are listed in Table 1.

(iii) *The three-dimensional structure.* As the (010)-projections turned out to be centrosymmetric the space group  $Cm$  could be excluded. By considering the interatomic distances on the basis of the parameters in the (010)-projections there appeared to be only one possible three-dimensional arrangement of the atoms. Apart from the minor deviations from the fixed  $y$ -values, 0 and  $\frac{1}{2}$ , of space group  $C2/m$  which are permitted in space group  $C2$ , the same three-dimensional arrangement is obtained in either of the two space groups.

Comparisons of  $F_o(h1l)$  and  $F_c(h1l)$  (Table 1) were performed in order to confirm the assumed structures. The highest symmetric space group  $C2/m$  was chosen and the values of  $x$ ,  $z$ , and  $B$  were assumed to be correctly obtained in

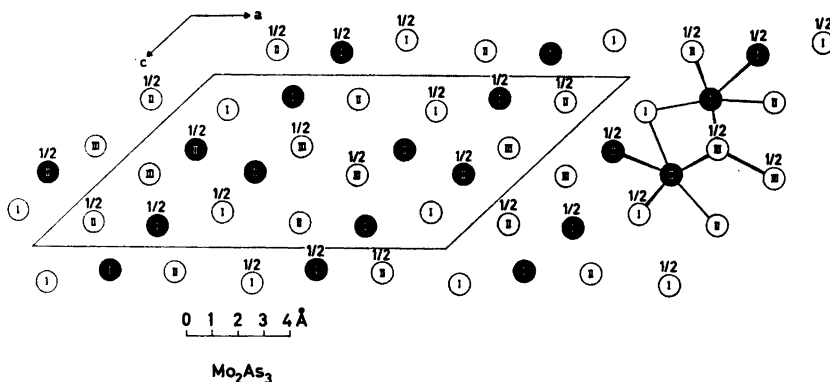


Fig. 2. The structure of  $\text{Mo}_2\text{As}_3$  ( $\text{W}_2\text{As}_3$ ) projected along [010]. Filled circles represent metal atoms and open circles represent metalloids. The numbers indicate fractions of the projection axis.

the (010)-projections.  $R$ -Values of 0.081 for  $\text{Mo}_2\text{As}_3$  and 0.091 for  $\text{W}_2\text{As}_3$  were obtained after corrections for secondary extinction, showing that the space group and atomic parameters were correctly chosen.

In terms of the space group  $C2/m$  all the atoms ( $T_{\text{I}}$ ,  $T_{\text{II}}$ ,  $\text{As}_{\text{I}}$ ,  $\text{As}_{\text{II}}$ , and  $\text{As}_{\text{III}}$ ) are in positions 4 (*i*), *i.e.*  $\pm(x, 0, z; \frac{1}{2}+x, \frac{1}{2}, z)$ , and the final values of  $x$ ,  $z$ , and  $B$  are listed in Table 2. The error limits indicated in the table correspond to twice the standard deviations obtained in the least-square calculations.  $\text{Mo}_2\text{As}_3$  and  $\text{W}_2\text{As}_3$  are accordingly isostructural with very similar lattice dimensions and atomic parameters. The structural arrangement in  $\text{Mo}_2\text{As}_3$  is shown in Fig. 2.

(iv) *Interatomic distances and coordinations.* The coordination around the Mo (W) and As atoms can be seen from Fig. 2; and the interatomic distances ( $< 4 \text{ \AA}$ ) and angles are listed in Table 3.

Each Mo (W) atom ( $T_{\text{I}}$  and  $T_{\text{II}}$  have nearly the same configuration of near neighbours) is surrounded by six As atoms at the corners of a somewhat distorted octahedron. The structures might be looked upon as built up by these  $T\text{As}_6$  octahedra coupled together by common edges. The  $T$  atoms are shifted from the centres of the  $\text{As}_6$  octahedra (towards one of the faces) in a manner which produces short  $T-T$  distances. The short  $T-T$  distances form planar zigzag chains of  $T_{\text{I}}-T_{\text{I}}$  and  $T_{\text{II}}-T_{\text{II}}$  atoms, linear chains of  $T_{\text{I}}-T_{\text{I}}$  and  $T_{\text{II}}-T_{\text{II}}$  atoms (parallel to  $[010]$ ), and pairs of  $T_{\text{I}}-T_{\text{II}}$  atoms (see Fig. 2 and Table 3). The interatomic  $T-T$  distances within the linear chains ( $3.2349 \pm 0.0004 \text{ \AA}$  in  $\text{Mo}_2\text{As}_3$  and  $3.2791 \pm 0.0004 \text{ \AA}$  in  $\text{W}_2\text{As}_3$ ) and the pairs ( $3.258 \pm 0.012 \text{ \AA}$  in  $\text{Mo}_2\text{As}_3$  and  $3.276 \pm 0.016 \text{ \AA}$  in  $\text{W}_2\text{As}_3$ ) are about  $0.3 \text{ \AA}$  longer than the corresponding distances within the zigzag chains ( $2.940 \pm 0.008 \text{ \AA}$  and  $2.955 \pm 0.006 \text{ \AA}$  in  $\text{Mo}_2\text{As}_3$  and  $2.934 \pm 0.010 \text{ \AA}$  and  $2.888 \pm 0.006 \text{ \AA}$  in  $\text{W}_2\text{As}_3$  for respectively the  $T_{\text{I}}-T_{\text{I}}$  and  $T_{\text{II}}-T_{\text{II}}$  distances). These  $T-T$  distances are somewhat longer than the corresponding distances of  $2.726 \text{ \AA}$  and  $2.741 \text{ \AA}$  in body centered molybdenum and tungsten metals.<sup>13</sup>

Each  $\text{As}_{\text{I}}$  and  $\text{As}_{\text{II}}$  atom is coordinated to four  $T$  atoms and each  $\text{As}_{\text{III}}$  atom is coordinated to four  $T$  atoms and one  $\text{As}_{\text{III}}$  atom. The arrangement of the  $\text{As}_{\text{III}}$  atoms produces pairs of  $\text{As}_{\text{III}}-\text{As}_{\text{III}}$  with short interatomic

Table 2. Final parameters for  $\text{Mo}_2\text{As}_3$  and  $\text{W}_2\text{As}_3$ .

Compound	Atom	$x$	$z$	$B (\text{\AA}^2)$
$\text{Mo}_2\text{As}_3$	$\text{Mo}_{\text{I}}$	$0.2482 \pm 0.0009$	$0.1252 \pm 0.0015$	$1.1 \pm 0.2$
	$\text{Mo}_{\text{II}}$	$0.3511 \pm 0.0009$	$0.5667 \pm 0.0015$	$1.2 \pm 0.2$
	$\text{As}_{\text{I}}$	$0.1270 \pm 0.0012$	$0.2069 \pm 0.0020$	$1.3 \pm 0.3$
	$\text{As}_{\text{II}}$	$0.4145 \pm 0.0013$	$0.1435 \pm 0.0021$	$1.4 \pm 0.3$
	$\text{As}_{\text{III}}$	$0.1035 \pm 0.0012$	$0.5795 \pm 0.0020$	$1.2 \pm 0.3$
$\text{W}_2\text{As}_3$	$\text{W}_{\text{I}}$	$0.2520 \pm 0.0012$	$0.1243 \pm 0.0020$	$2.2 \pm 0.4$
	$\text{W}_{\text{II}}$	$0.3485 \pm 0.0012$	$0.5672 \pm 0.0020$	$2.1 \pm 0.4$
	$\text{As}_{\text{I}}$	$0.1249 \pm 0.0027$	$0.2033 \pm 0.0048$	$1.7 \pm 0.7$
	$\text{As}_{\text{II}}$	$0.4168 \pm 0.0029$	$0.1457 \pm 0.0051$	$1.8 \pm 0.7$
	$\text{As}_{\text{III}}$	$0.1051 \pm 0.0027$	$0.5796 \pm 0.0050$	$1.6 \pm 0.7$



Table 3. Interatomic distances and angles in  $\text{Mo}_2\text{As}_3$  and  $\text{W}_2\text{As}_3$ . (The indicated error limits correspond to those listed for the parameters in Table 2.)

Interatomic distances (Å)					
	$\text{Mo}_2\text{As}_3$	$\text{W}_2\text{As}_3$		$\text{Mo}_2\text{As}_3$	$\text{W}_2\text{As}_3$
$T_{\text{I}}$	$-2T_{\text{I}}$	$2.940 \pm 0.008$	$\text{As}_{\text{I}}$	$3.346 \pm 0.014$	$3.334 \pm 0.032$
	$-2T_{\text{I}}$	$3.2349 \pm 0.0004$	$-2\text{As}_{\text{III}}$	$3.551 \pm 0.009$	$3.543 \pm 0.021$
	$-T_{\text{II}}$	$3.258 \pm 0.012$	$-T_{\text{I}}$	$3.877 \pm 0.013$	$3.848 \pm 0.031$
$T_{\text{II}}$	$-T_{\text{I}}$	$2.579 \pm 0.007$	$\text{As}_{\text{II}}$	$2.510 \pm 0.012$	$2.532 \pm 0.025$
	$-2\text{As}_{\text{II}}$	$2.510 \pm 0.012$	$-T_{\text{I}}$	$2.545 \pm 0.007$	$2.549 \pm 0.011$
	$-T_{\text{II}}$	$2.545 \pm 0.007$	$-T_{\text{II}}$	$2.580 \pm 0.014$	$2.573 \pm 0.028$
	$-2\text{As}_{\text{III}}$	$2.554 \pm 0.013$	$-2\text{As}_{\text{I}}$	$3.405 \pm 0.008$	$3.371 \pm 0.013$
	$-T_{\text{I}}$	$3.909 \pm 0.016$	$-2\text{As}_{\text{I}}$	$3.346 \pm 0.014$	$3.334 \pm 0.032$
	$-2T_{\text{II}}$	$3.258 \pm 0.012$	$-2\text{As}_{\text{I}}$	$3.2349 \pm 0.0004$	$3.2791 \pm 0.0004$
	$-2T_{\text{II}}$	$2.955 \pm 0.006$	$-2\text{As}_{\text{III}}$	$3.311 \pm 0.012$	$3.331 \pm 0.027$
	$-2T_{\text{II}}$	$3.2349 \pm 0.0004$	$-2\text{As}_{\text{III}}$	$3.305 \pm 0.017$	$3.296 \pm 0.041$
	$-2\text{As}_{\text{I}}$	$2.527 \pm 0.010$	$-T_{\text{I}}$	$3.869 \pm 0.019$	$3.869 \pm 0.044$
	$-T_{\text{I}}$	$2.609 \pm 0.015$	$\text{As}_{\text{III}}$	$2.554 \pm 0.013$	$2.564 \pm 0.027$
$\text{As}_{\text{I}}$	$-T_{\text{II}}$	$2.580 \pm 0.014$	$-T_{\text{I}}$	$2.909 \pm 0.016$	$3.898 \pm 0.033$
	$-2\text{As}_{\text{III}}$	$2.576 \pm 0.007$	$-2T_{\text{II}}$	$2.576 \pm 0.007$	$2.597 \pm 0.014$
	$-T_{\text{I}}$	$2.579 \pm 0.007$	$-2\text{As}_{\text{I}}$	$3.551 \pm 0.009$	$3.543 \pm 0.021$
	$-2T_{\text{II}}$	$2.527 \pm 0.010$	$-T_{\text{I}}$	$3.877 \pm 0.013$	$3.848 \pm 0.031$
	$-T_{\text{II}}$	$2.609 \pm 0.015$	$-2\text{As}_{\text{II}}$	$3.311 \pm 0.012$	$3.331 \pm 0.027$
	$-T_{\text{I}}$	$2.976 \pm 0.017$	$-2\text{As}_{\text{I}}$	$3.305 \pm 0.017$	$3.296 \pm 0.041$
	$-2\text{As}_{\text{I}}$	$3.2349 \pm 0.0004$	$-T_{\text{I}}$	$2.445 \pm 0.010$	$2.477 \pm 0.022$
	$-2\text{As}_{\text{I}}$	$3.405 \pm 0.008$	$-2\text{As}_{\text{III}}$	$3.2349 \pm 0.0004$	$3.2791 \pm 0.0004$

Table 3. Continued.

Interatomic angles ( $^{\circ}$ ) (other than 90 and 180 $^{\circ}$ )

		Mo <sub>2</sub> As <sub>3</sub>	W <sub>2</sub> As <sub>3</sub>		Mo <sub>2</sub> As <sub>3</sub>	W <sub>2</sub> As <sub>3</sub>
As <sub>I</sub> - T <sub>I</sub>	-	As <sub>II</sub>	81.6 ± 0.6	As <sub>II</sub> - T <sub>II</sub>	79.7 ± 0.3	79.2 ± 0.6
	-	As <sub>II</sub>	165.1 ± 2.6	As <sub>III</sub> - T <sub>II</sub>	77.8 ± 0.2	78.3 ± 0.2
	-	As <sub>III</sub>	87.6 ± 0.3	T <sub>I</sub> - T <sub>I</sub>	66.7 ± 0.2	68.0 ± 0.3
As <sub>II</sub> - T <sub>I</sub>	-	As <sub>II</sub>	80.7 ± 0.4	-	141.1 ± 0.9	140.9 ± 1.2
	-	As <sub>II</sub>	108.9 ± 0.4	T <sub>I</sub> - T <sub>II</sub>	94.6 ± 0.2	94.2 ± 0.3
	-	As <sub>III</sub>	99.6 ± 0.5	T <sub>II</sub> - T <sub>II</sub>	66.4 ± 0.2	69.2 ± 0.2
As <sub>III</sub> - T <sub>I</sub>	-	As <sub>III</sub>	81.0 ± 0.3	T <sub>I</sub> - As <sub>I</sub>	77.8 ± 0.3	78.4 ± 0.7
	-	As <sub>III</sub>	78.6 ± 0.4	T <sub>II</sub> - As <sub>I</sub>	70.2 ± 0.3	68.5 ± 0.5
As <sub>I</sub> - T <sub>II</sub>	-	As <sub>I</sub>	79.6 ± 0.2	T <sub>I</sub> - As <sub>II</sub>	71.1 ± 0.3	70.5 ± 0.4
	-	As <sub>I</sub>	109.8 ± 0.6	T <sub>I</sub> - As <sub>III</sub>	78.9 ± 0.3	78.8 ± 0.7
	-	As <sub>II</sub>	83.6 ± 0.3			
	-	As <sub>II</sub>	162.2 ± 3.3			
	-	As <sub>III</sub>	86.5 ± 0.3			
	-	As <sub>III</sub>	98.9 ± 0.4			

distances. The  $\text{As}_{\text{III}}-\text{As}_{\text{III}}$  distances of  $2.445 \pm 0.010$  Å and  $2.477 \pm 0.022$  Å in, respectively,  $\text{Mo}_2\text{As}_3$  and  $\text{W}_2\text{As}_3$  are in good agreement with the expectation value of  $2.49 \pm 0.08$  Å for the single bond As—As distance suggested by Furuseth *et al.*<sup>14</sup>

(v) *Application of the general (8-N) rule.* The observed interatomic distances indicate that  $T-T$  and As—As bonds as well as the  $T$ —As bonds exist in  $T_2\text{As}_3$ . The significance of these  $T-T$  and As—As bonds can be discussed in terms of the general (8-N) rule.<sup>15-20</sup> The usual form of this rule is a mathematical formulation of the need for all the anions in a crystal to have complete octets:<sup>17</sup>

$$(n + P - Q)/a = 8$$

where  $n$  is the total number of valence electrons (excluding any unshared electrons on the cations);  $P$  is the number of electrons involved in forming anion—anion bonds;  $Q$  is the number of electrons involved in forming cation—cation bonds;  $a$  is the number of anions, all these values being calculated per formula unit of the compound.

The following values of  $n$ ,  $P$ ,  $Q$ , and  $a$  are estimated from the available experimental data for  $\text{Mo}_2\text{As}_3$  and  $\text{W}_2\text{As}_3$ . (More detailed considerations regarding valence ( $n$ ), crystal structure ( $P$  and  $Q$ ), composition ( $a$ ), and electronic band structure (8) are given by Kjekshus.<sup>20</sup>):

$n = 27$ . Each  $T$  atom is assumed to contribute 6 electrons and each As atom 5 electrons to  $n$ , *i.e.* the valence states of the constituent atoms correspond to their group numbers in the Periodic Table. The present experience justifies the assumed number of 5 valence electrons per As atom and gives fairly strong support for the assumption concerning 6 valence electrons per  $T$  atom.<sup>20</sup> The observed diamagnetism<sup>4</sup> of  $\text{Mo}_2\text{As}_3$  and  $\text{W}_2\text{As}_3$ , *i.e.* no localized unpaired  $d$ -electrons on the  $T$  atoms, is furthermore consistent with 6 valence electrons per  $T$  atom. (4 and 2 valence electrons per  $T$  atom are, however, equally valid possibilities according to the magnetic measurements.)

$P = 1$ . Each short  $\text{As}_{\text{III}}-\text{As}_{\text{III}}$  distance (see Fig. 2) is counted as one shared electron pair, *i.e.* 1 electron per  $\text{As}_{\text{III}}$  atom is involved in forming As—As bonds. (No bonding interaction is assumed to be present between As atoms separated by distances  $\geq 2.9$  Å; *cf.* Table 3.)

$Q = 4$ . Each short  $T_{\text{I}}-T_{\text{I}}$  and  $T_{\text{II}}-T_{\text{II}}$  distance (within the planar  $T-T$  zigzag chains, see Fig. 2) is counted as one shared electron pair, *i.e.* 2 electrons per  $T$  atom are involved in forming  $T-T$  bonds. It has on the other hand been assumed that the linear  $T_{\text{I}}-T_{\text{I}}$  and  $T_{\text{II}}-T_{\text{II}}$  chains and the  $T_{\text{I}}-T_{\text{II}}$  pairs are caused by the geometry of the crystal structure.

$a = 3$ . The composition is unequivocally determined to be  $T_2\text{As}_3$ .<sup>4</sup>

The values  $n = 27$ ,  $P = 1$ ,  $Q = 4$ , and  $a = 3$  satisfy the equation  $(n + P - Q)/a = 8$ ; *i.e.* the general (8-N) rule is fulfilled.  $\text{Mo}_2\text{As}_3$  and  $\text{W}_2\text{As}_3$  may accordingly be regarded, and listed, as polyanionic—polycationic valence compounds and furthermore at first sight be expected to be semiconductors. The latter prediction is, however, somewhat doubtful in view of the arrangement of the  $T$  atoms in the  $T_2\text{As}_3$  structure.  $\text{Mo}_2\text{As}_3$  and  $\text{W}_2\text{As}_3$  will be more likely to exhibit metallic type of conductivity resulting from the  $T_{\text{I}}-T_{\text{I}}$  and  $T_{\text{II}}-T_{\text{II}}$  chains running continuously throughout the  $T_2\text{As}_3$  structure (*cf.* Refs. 15-17, and 19).

(vi) *Structural relationships.* The  $\text{Mo}_2\text{As}_3$  ( $\text{W}_2\text{As}_3$ ) structure can be classified among the structure types having octahedral coordination of the metal atoms. A large number of binary transition metal compounds (usually with a composition between 50.00 and 66.67 atomic % metalloid) crystallizes with structures belonging to this class. Common structure types with octahedral coordination of the metal atoms are, *e.g.*, the NiAs (including the closely-related structure types with random and ordered distribution of vacancies in the metal sublattice), MnP,  $\text{Cd}(\text{OH})_2$ ,  $\text{FeS}_2$  (pyrite),  $\text{FeS}_2$  (marcasite), and  $\text{CoSb}_2$  ( $\text{FeAsS}$ , arsenopyrite) structures. (Binary transition metal compounds crystallizing with these structure types are, *e.g.*, listed by Refs. 19–22.) More rare structure types with octahedral coordination around the metal atoms are, *e.g.*, the  $\text{Nb}_3\text{Te}_4$  ( $\text{Nb}_3\text{Se}_4$ ),<sup>23</sup>  $\text{Mo}_2\text{S}_3$ ,<sup>24</sup>  $\text{NbTe}_2$  ( $\text{TaTe}_2$ ),<sup>25</sup>  $\beta\text{-MoTe}_2$ ,<sup>26</sup>  $\text{WTe}_2$ ,<sup>26</sup>  $\text{ReSe}_2$ ,<sup>27</sup> and  $\text{IrSe}_2$ <sup>28</sup> structures. Each of the above mentioned structure types may be regarded as being built up of metalloid octahedra, the stacking of these octahedra and the fitting of the metal atoms into the octahedral interstices may differ in the various types.

Further classification is obtained in the description of the above mentioned structure types by listing them in four sub-classes:

- (1)  $P = 0, Q = 0$   $\text{Cd}(\text{OH})_2$ , some representatives of the NiAs family.
- (2)  $P \neq 0, Q = 0$   $\text{FeS}_2(\text{p})$ ,  $\text{FeS}_2(\text{m})$ ,  $\text{IrSe}_2$ .
- (3)  $P = 0, Q \neq 0$  MnP,  $\text{Nb}_3\text{Te}_4$ ,  $\text{Mo}_2\text{S}_3$ ,  $\beta\text{-MoTe}_2$ ,  $\text{WTe}_2$ ,  $\text{ReSe}_2$ , some representatives of the NiAs family,  $\text{NbTe}_2(?)$ .
- (4)  $P \neq 0, Q \neq 0$   $\text{CoSb}_2$ ,  $\text{Mo}_2\text{As}_3$ , "compressed"  $\text{FeS}_2(\text{m})$ .

It must be emphasized that this classification is based purely on considerations of the interatomic distances in the crystal structures and does not necessarily imply that the general (8–N) rule is satisfied. (Further details regarding the application of the general (8–N) rule to compounds with these types of crystal structures are published elsewhere.<sup>20</sup>) As the  $\text{Mo}_2\text{As}_3$  ( $\text{W}_2\text{As}_3$ ) structure belongs to sub-class 4 it has certain structural features in common with those of sub-classes 2, 3, and 4. The structural relationships between the  $\text{Mo}_2\text{As}_3$  ( $\text{W}_2\text{As}_3$ ) structure and most of the other structure types are, however, not very marked. (A more detailed discussion of the relationships between the structures of transition metal compounds will be published elsewhere.<sup>20</sup>)

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