

## The Crystal Structure of $\text{Mo}_5\text{As}_4$

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$\text{Mo}_5\text{As}_4$  has a tetragonal  $\text{Ti}_5\text{Te}_4$  type structure with unit cell dimensions  $a = 9.6005 \pm 0.0006 \text{ \AA}$ ,  $c = 3.2781 \pm 0.0004 \text{ \AA}$ . The space group is  $I4/m$  with  $2\text{Mo}_I$  in  $(a)$  with  $B = 0.95 \text{ \AA}^2$ ,  $8\text{Mo}_{II}$  in  $(h)$  with  $x_1 = 0.2996$ ,  $y_1 = 0.3752$ ,  $B_1 = 1.12 \text{ \AA}^2$ , and  $8\text{As}$  in  $(h)$  with  $x_2 = 0.0507$ ,  $y_2 = 0.2863$ ,  $B_2 = 1.65 \text{ \AA}^2$ . Crystals of  $\text{Mo}_5\text{As}_4$  are twinned along  $\{100\}$ .

In previous communications<sup>1-5</sup> on the crystal chemistry of molybdenum arsenides and antimonides, the structures of  $\text{Mo}_2\text{As}_3$ ,  $\text{MoAs}_2$ , and  $\text{Mo}_3\text{Sb}_7$  have been described. In this paper we present data on the crystal structure of  $\text{Mo}_5\text{As}_4$ .

The existence of the  $\text{Mo}_5\text{As}_4$  phase has recently been established as result of independent studies by Boller and Nowotny,<sup>6</sup> Taylor *et al.*,<sup>7</sup> and Jensen *et al.*<sup>3</sup> Boller and Nowotny reported that  $\text{Mo}_5\text{As}_4$  crystallizes with the  $\text{Ti}_5\text{Te}_4$  type structure or a somewhat modified form thereof (see below) on the basis of comparisons of calculated and observed intensities of X-ray powder photograph data. Taylor *et al.* assigned the  $\text{Ti}_5\text{Te}_4$  type structure to  $\text{Mo}_5\text{As}_4$  without publishing data supporting this statement; which apparently seems to be a semi-quotation from Boller and Nowotny.

### RESULTS

(i) *Unit cell and space group.* According to Jensen *et al.*<sup>3</sup> the unit cell of  $\text{Mo}_5\text{As}_4$  is tetragonal with the following dimensions:

$$a = 9.6005 \pm 0.0006 \text{ \AA}, c = 3.2781 \pm 0.0004 \text{ \AA}$$

The lattice dimensions are calculated from Guinier photograph data (taken with strictly monochromatized  $\text{CuK}\alpha_1$  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 deviation obtained in these calculations.

The composition  $\text{Mo}_5\text{As}_4$  was determined by using the disappearing phase principle on Guinier photograph data and by application of the thermal

decomposition method. No extended range of homogeneity of this phase exists.

On the basis of the observed density  $8.48 \text{ g cm}^{-3}$  (at  $25.00^\circ\text{C}$ ), the unit cell contains  $2(Z_c = 1.98) \text{ Mo}_5\text{As}_4$ -groups.

A large number of apparently single crystals of  $\text{Mo}_5\text{As}_4$  was obtained by means of chemical transport reactions using traces of bromine (chlorine or iodine) as transport agent. The needle-shaped crystals had approximately square cross-section with  $[001]$  parallel to the needle axis.

The only systematically missing reflections in the Guinier and Weissenberg photographs were of the type  $(hkl)$  absent when  $h + k + l = 2n + 1$  showing a body-centered unit cell. The Weissenberg photographs indicated furthermore Laue group  $4/mmm$ . However, at a later stage it was discovered (see ii below) that the crystals were twinned with twin plane  $\{100\}$ . (The twinning is probably lamellar.) The true Laue group turned out to be  $4/m$  and the space group is  $I4/m$ .

(ii) *Determination of the structure.* Intensity measurements of the  $hk0$  and  $hkl$  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  $\text{CuK}$ -radiation. The cross-section of the crystal used for these measurements was  $0.007 \times 0.007 \text{ mm}^2$ .) The intensities were corrected for the combined Lorentz and polarization factor. The correction for absorption was neglected since  $\mu R$  would be  $\sim 0.4$  if the shape of the crystal is assumed to be cylindrical. For the calculation of  $F_c$ -values the atomic scattering factors were taken from *International Tables*.<sup>8</sup>

The tetragonal structure (Fig. 1) of a phase  $\text{Ti}_5\text{Te}_4$  has been described by Grønvold *et al.*<sup>9</sup> Six other binary phases are also shown<sup>6,10-14</sup> to be isostructural with  $\text{Ti}_5\text{Te}_4$ , i.e.  $\text{V}_5\text{S}_4$ ,  $\text{V}_5\text{Se}_4$ ,  $\text{Nb}_5\text{Se}_4$ ,  $\text{Nb}_5\text{Te}_4$ ,  $\text{Nb}_5\text{Sb}_4$ , and  $\text{Ta}_5\text{Sb}_4$ . A  $\text{Ti}_5\text{Te}_4$  type structure has furthermore been proposed for  $\text{Mo}_5\text{As}_4$  by Boller and Nowotny<sup>6</sup> and Taylor *et al.*<sup>7</sup> The obvious relationship in composition and similar unit cell dimensions of these phases indicate that this suggestion is

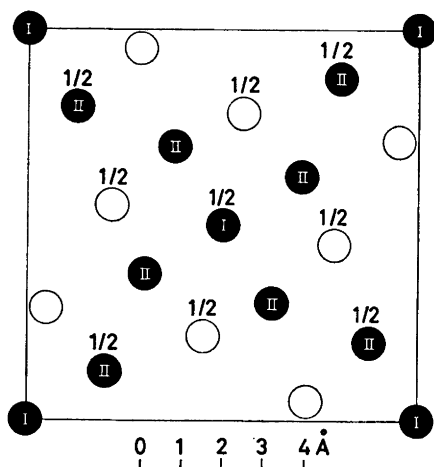


Fig. 1. The  $\text{Ti}_5\text{Te}_4$  type structure of  $\text{Mo}_5\text{As}_4$  projected along  $[001]$ . Filled circles represent Mo atoms and open circles represent As atoms. The numbers indicate fractions of the projection axis.

correct. The observed intensities on the Weissenberg photographs (showing  $I(hkl) = I(khl)$ ) suggested on the other hand Laue group  $4/mmm$  rather than  $4/m$ , *i.e.* inconsistent with the space group  $I4/m$  of the  $\text{Ti}_5\text{Te}_4$  structure. Two reasons were considered in order to account for this inconsistency:

(1) It is possible to rearrange the atoms in the  $\text{Ti}_5\text{Te}_4$  structure in agreement with a higher symmetric space group, *e.g.*  $I4/mmm$ . However, fairly large shifts of the  $\text{Ti}_{\text{II}}$  and Te atoms in positions  $8(h)$  are necessary in order to obtain the symmetry of space group  $I4/mmm$ .

(2) The crystal may be a twin. If the twins are of equal size with twin plane  $\{100\}$ , the observed intensity of each reflection on the Weissenberg photographs would be the sum of  $I(hkl)$  of twin A and  $I(khl)$  of twin B. The observed relationship  $I(hkl) = I(khl)$  may accordingly be accounted for.

At this stage it was decided to try to distinguish between the two possibilities by means of a Patterson projection on the basis of the corrected  $F_o^2(hk0)$  values. The Patterson map excluded immediately the first possibility, whereas it was essentially consistent with the second. All the peaks in the map (the locations as well as the relative heights) could be accounted for assuming that it is produced by two superimposed  $\text{Ti}_5\text{Te}_4$  type unit cells, one being the mirror-image of the other. The twin hypothesis was therefore considered as proved.

Despite numerous attempts it was impossible to find a true single crystal, all crystals tested were invariably twins obeying the relationship  $I(hkl) = I(khl)$ .

Further examination of the structure was accordingly based on the intensity data already collected for the first crystal. These data could evidently not be analysed in the conventional way. However, the intensities of the  $h00$  and  $hh0$  reflections must be unaffected of the twinning, and this fact could be utilized in the evaluation of the atomic parameters. A comparison of  $F_o$  and  $F_c$  (based on the parameter values of  $\text{Ti}_{\text{II}}$  and Te found in the crystal structure of  $\text{Ti}_5\text{Te}_4$ ) of these reflections indicates the correctness of the assumed  $\text{Ti}_5\text{Te}_4$  type structure for  $\text{Mo}_5\text{As}_4$ . Further improvement of the atomic parameters was obtained by least-square refinement using the same reflections for these calculations.

The deduced atomic arrangement (Fig. 1) is in terms of space group  $I4/m$  as follows:

$$\begin{array}{ll} 2\text{Mc}_{\text{I}} \text{ in } (a) \text{ with} & B = 0.95 \text{ \AA}^2 \\ 8\text{Mo}_{\text{II}} \text{ in } (h) \text{ with } x_1 = 0.2996, y_1 = 0.3752, B_1 = 1.12 \text{ \AA}^2 & \\ 8\text{As} \text{ in } (h) \text{ with } x_2 = 0.0507, y_2 = 0.2863, B_2 = 1.65 \text{ \AA}^2 & \end{array}$$

The derived values of  $x$ ,  $y$ , and  $B$  were tested using the data for all  $hk0$  and  $hk1$  reflections. The reliability indices

$$\begin{aligned} R^* &= \frac{\sum |F_o^2 - F_c^2|}{\sum F_o^2} \text{ and} \\ R^{**} &= \frac{\sum ||\sqrt{F_o^2} - \sqrt{F_c^2}||}{\sum \sqrt{F_o^2}} \end{aligned}$$

were calculated in order to judge the accordance between the observed and calculated data ( $F_c^2 = F_c^2(hkl) + F_c^2(khl)$ ).  $R^* = 0.14$  and  $R^{**} = 0.095$  were obtained for the  $hk0$  reflections and  $R^* = 0.15$  and  $R^{**} = 0.106$  were

found for the  $hkl$  reflections. The  $F_o^2$  and  $F_c^2$  values are listed in Table 1. The agreement is so good that the proposed structure and selected parameter values must be correct.

For the purpose of comparison it may be mentioned that the parameter values reported by Boller and Nowotny<sup>6</sup> for  $\text{Mo}_5\text{As}_4$  gave  $R^* = 0.45$  using the present  $F_o^2(hk0)$  data, whereas the parameter values found by Grønvold *et al.*<sup>9</sup> for  $\text{Ti}_5\text{Te}_4$  gave  $R^* = 0.42$ . ( $B = 0.5 \text{ \AA}^2$  for all atoms was chosen for these calculations. The present values of  $x_1$ ,  $y_1$ ,  $x_2$ , and  $y_2$  gave  $R^* = 0.21$  for the  $hk0$  reflections using  $B = 0.5 \text{ \AA}^2$  for all atoms.) Boller and Nowotny have furthermore introduced the possibility of a somewhat modified  $\text{Ti}_5\text{Te}_4$  type structure for  $\text{Mo}_5\text{As}_4$ . This modification consists of interchanging the coordinates of  $\text{Mo}_{\text{II}}$  and As. Similar least-square refinement to that described above gave  $B = 1.45 \text{ \AA}^2$ ,  $x_1 = 0.0504$ ,  $y_1 = 0.2860$ ,  $B_1 = 2.98 \text{ \AA}^2$ ,  $x_2 = 0.2981$ ,  $y_2 = 0.3751$ , and  $B_2 = 0.04 \text{ \AA}^2$  with  $R^* = 0.21$  for the  $hk0$  reflections. The comparatively low value of  $R^*$  (nevertheless significantly higher than that

Table 1. Observed and calculated structure factor data for  $\text{Mo}_5\text{As}_4$ .

$hkl$	$F_o^2$	$F_c^2 \times 10^{-2}$	$hkl$	$F_o^2$	$F_c^2 \times 10^{-2}$	$hkl$	$F_o^2$	$F_c^2 \times 10^{-2}$
200	86	67	1130	73	66	611	92	106
400	72	81	440	0	1	811	65	97
600	52	26	640	26	16	1011	78	85
800	0	4	840	210	151	321	265	322
1000	144	122	1040	124	153	521	187	232
1200	112	236	550	106	112	721	666	735
110	240	182	750	506	486	921	284	297
310	45	34	950	236	248	1121	89	59
510	420	427	1150	48	68	431	50	45
710	448	537	660	47	39	631	29	35
910	149	122	860	96	84	831	20	24
1100	76	68	1060	12	25	1031	105	75
220	169	151	770	211	158	541	432	518
420	1323	1313	970	24	13	741	207	165
620	668	537	880	29	35	941	0	4
820	153	159	301	2375	2558	1141	213	106
1020	121	154	501	66	44	651	439	398
1220	27	87	701	114	113	851	115	89
330	1234	1367	901	439	268	1051	180	174
530	327	313	1101	48	29	761	53	36
730	85	87	211	389	420	961	54	24
930	121	96	411	541	578	871	218	179

obtained for the corresponding unmodified arrangement) is undoubtedly due to the small difference in the X-ray scattering factors of Mo and As, and this alternative was accordingly disregarded.

(iii) *Interatomic distances.* The interatomic distances between nearest neighbours calculated from the parameter values given above are listed in Table 2. The short Mo—As distances in  $\text{Mo}_5\text{As}_4$  (ranging from  $2.49_1 \text{ \AA}$  to

Table 2. Interatomic distances in  $\text{Mo}_5\text{As}_4$  (Å).

$\text{Mo}_I$	— $2\text{Mo}_I$	: 3.278 <sub>1</sub>	$\text{As}$	— $1\text{Mo}_I$	: 2.79 <sub>1</sub>
	— $8\text{Mo}_{II}$	: 2.79 <sub>7</sub>		— $2\text{Mo}_{II}$	: 2.49 <sub>1</sub>
	— $4\text{As}$	: 2.79 <sub>1</sub>		— $1\text{Mo}_{II}$	: 2.53 <sub>8</sub>
$\text{Mo}_{II}$	— $2\text{Mo}_I$	: 2.79 <sub>7</sub>		— $2\text{Mo}_{II}$	: 2.67 <sub>5</sub>
	— $2\text{Mo}_{II}$	: 3.06 <sub>8</sub>		— $2\text{As}$	: 3.278 <sub>1</sub>
	— $2\text{Mo}_{II}$	: 3.20 <sub>5</sub>		— $4\text{As}$	: 3.77 <sub>4</sub>
	— $2\text{Mo}_{II}$	: 3.278 <sub>1</sub>		— $2\text{As}$	: 3.94 <sub>8</sub>
	— $2\text{As}$	: 2.49 <sub>1</sub>			
	— $1\text{As}$	: 2.53 <sub>8</sub>			
	— $2\text{As}$	: 2.67 <sub>5</sub>			

2.79<sub>1</sub> Å) are of the same size as those found in  $\text{Mo}_2\text{As}_3$  <sup>4</sup> ( $2.510 \pm 0.012$  Å —  $2.609 \pm 0.015$  Å) and  $\text{MoAs}_2$  <sup>15</sup> ( $2.524 \pm 0.007$  Å —  $2.672 \pm 0.005$  Å). The shortest Mo—Mo distance in  $\text{Mo}_5\text{As}_4$  (2.79<sub>7</sub> Å) is considerably shorter than the corresponding distances in  $\text{Mo}_2\text{As}_3$  ( $2.940 \pm 0.008$  Å and  $2.955 \pm 0.006$  Å) and  $\text{MoAs}_2$  ( $3.002 \pm 0.005$  Å), whereas it compares fairly well with the shortest Mo—Mo distance of 2.726 Å in body-centered Mo metal.<sup>16</sup> (The coordination of  $\text{Mo}_{II}$  atoms around  $\text{Mo}_I$  is the same as in Mo metal.) The shortest As—As distance in  $\text{Mo}_5\text{As}_4$  is much larger than similar distances in the other molybdenum arsenides ( $2.445 \pm 0.010$  Å in  $\text{Mo}_2\text{As}_3$  and  $2.412 \pm 0.001$  Å in  $\text{MoAs}_2$ ).

For a detailed description of the structure reference is made to Grønvold *et al.*<sup>9</sup>

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