

different atoms, there may also be differences for atoms of the same type in different chemical configuration; no account is taken, for example, of the difference between a single carbon atom and carbon in a methyl group. In sign determination, these errors are important only for reflexions at small angles, and of small amplitude.

Experimental determinations have been checked against normal computational methods and in a typical example out of 126 reflexions only 17 were found to have doubtful signs. These reflexions had an amplitude less than 5% of the maximum observed and, as pointed out earlier, would not be included in a Fourier synthesis.

The method has now been used in this department on a number of unknown structures, e.g. purpurogallin (Taylor, 1952*b*), triphenylene (Pinnock, Taylor & Lipson, 1955), bishydroxydurylmethane (Chaudhuri & Hargreaves, 1955), and is at present being used on a number of other structures as yet incompletely determined.

### APPENDIX I

Formula for the Leitz two-bath developer as quoted in *Wall's Dictionary of Photography* under 'Fine-grain development':

<i>Bath 1</i>	
Metol	5 g.
Sodium sulphite (anhydrous)	100 g.
(or Sodium sulphite (7 H <sub>2</sub> O))	200 g.)
Water	to 1000 cm. <sup>3</sup>

<i>Bath 2</i>	
Borax	10 g.
Water	to 1000 cm. <sup>3</sup>

Develop 3–6 min. in Bath 1 and 2–4 min. in Bath 2.

We wish to thank Prof. H. Lipson for valuable advice and helpful discussions. One of us (P. R. P.) acknowledges with thanks a maintenance grant from the Department of Scientific and Industrial Research.

### References

- CHAUDHURI, B. & HARGREAVES, A. (1955). In preparation.
- HANSON, A. W., LIPSON, H. & TAYLOR, C. A. (1953). *Proc. Roy. Soc. A*, **218**, 371.
- LIPSON, H. & TAYLOR, C. A. (1951). *Acta Cryst.* **4**, 458.
- PINNOCK, P. R., TAYLOR, C. A. & LIPSON, H. (1955). *Acta Cryst.* In the Press.
- TAYLOR, C. A. (1952*a*). *Acta Cryst.* **5**, 141.
- TAYLOR, C. A. (1952*b*). *Nature, Lond.* **169**, 1088.
- Wall's Dictionary of Photography*. London: Iliffe.
- ZERNIKE, F. (1946). *La Théorie des Images Optiques*. Paris: Centre National de la Recherche Scientifique.

*Acta Cryst.* (1955). **8**, 691

## The Structure of MoBe<sub>12</sub>\*

BY RICHARD F. RAEUCHLE AND FRED W. VON BATCHELDER

*Naval Research Laboratory, Washington 25, D.C., U.S.A.*

(Received 19 January 1955 and in revised form 1 March 1955)

The structure of MoBe<sub>12</sub> has been determined. Formal valences of 3.36 for molybdenum and 1.85, 2.27 and 2.59 for beryllium have been calculated using Pauling's single-bonded metallic radii, and are interpreted in terms of electron shift.

### Introduction

In recent years considerable attention has been given to intermetallic compounds of the type  $MX_{12}$  and  $MX_{13}$ . Most structures investigated have been complex (such as ZrBe<sub>13</sub> (Baenziger & Rundle, 1949), and TiBe<sub>12</sub> (Raeuchle & Rundle, 1952)). The structure of the latter, in fact, is not yet completely known. When, therefore, the opportunity arose to study the molybdenum analog, which promised to be simpler, a structural study was undertaken in the hope of finding an underlying structural principle for this group of compounds.

The Mo–Be compound was first reported by Gordon, McGurty, Klein & Koshuba (1951). Although our samples were obtained from ingots prepared by Gordon and Koshuba, there is some doubt as to the actual identity of the two compounds. Chemical analysis showed the composition of the crystals used in the present investigation to be MoBe<sub>12</sub>, while Gordon *et al.* reported MoBe<sub>13</sub>. The structural analysis subsequently confirmed our composition for the samples studied. Their lattice constants indicated a unit cell which, if it had the structure found by us, would be face centered. (We have chosen a smaller cell which is body centered.) There is, however, good agreement between our lattice constants and theirs, when transformed to identical axes. We find the space group to

\* First reported at the American Crystallographic Association meeting in Chicago in October 1951.

be  $I4/mmm$ , as compared with a probable space group of  $P42$  given by Gordon *et al.* Had our crystals not been received from Gordon and Koshuba, the evidence would seem to indicate that our crystals and theirs were not identical. We have, however, found no phase present in the single crystals isolated from the ingot other than the MoBe<sub>12</sub> crystals reported on here.

### Experimental

Portions of a small ingot containing MoBe<sub>12</sub> were obtained from Gordon and Koshuba at the Fairchild Engine and Airplane Corporation in Oak Ridge. Crystalline fragments were separated by an electrolytic etch in very dilute HCl with the compound as anode. A few of the fragments which fell off the ingot proved to be single crystals. The single crystals, so obtained, showed no facial development that could be used for orientation, but several specimens were successfully oriented on the precession camera.

The crystals which ultimately proved to be single individuals were approximately 0.05 mm. in cross section. Larger fragments proved to be twinned, as will be discussed later. The orientation work on these small specimens was slow, and a sample mounted on the goniometer head in an undesirable orientation could not readily be remounted. This accounts for the choice, mentioned later, of [110] as a Weissenberg axis for intensity measurements.

The lattice constants and space group were determined from precession diagrams around  $a_0$  and  $c_0$ . The crystals are tetragonal, and since only the absences characteristic of body centering occurred, the space group is  $I4/mmm-D_{4h}^{17}$  or a subgroup.

The lattice constants, using  $\lambda(\text{Mo } K\alpha) = 0.7107 \text{ \AA}$ , were found to be:

$$a_0 = 7.271 \pm 0.005, \quad c_0 = 4.234 \pm 0.005 \text{ \AA},$$

which may be compared with the Gordon *et al.* (1951) values, transformed to our axes, of  $a = 7.28$ ,  $c = 4.29 \text{ \AA}$ . With  $Z = 2$  the density calculated for MoBe<sub>12</sub> is 3.02 g.cm.<sup>-3</sup>. Gordon *et al.* report the measured density as 3.13 g.cm.<sup>-3</sup>.

Single-crystal Weissenberg photographs were made around [001] and [110]. Weissenberg photographs around [100] would have been desirable, but [110] served the same purpose and a larger crystal more suitable for obtaining intensity data was found to be orientable around this axis. Filtered Mo  $K\alpha$  radiation was used and, although intensity photographs were taken for several layer lines around each axis, only ( $hk0$ ) and ( $hhl$ ) were needed in the structural determination and only these are reported here.

Intensity observations were made using timed exposures with an exposure factor of 4 and a standard comparison strip containing a series of 1° Weissenberg exposures with a factor of 2 between adjacent spots. Intensities were then estimated visually. Squares of the structure factors were calculated by the formula

$$I = K|F|^2G,$$

where  $G$  is the Lorentz polarization factor, and  $K$  is a constant, ultimately adjusted to give the best agreement between observed and calculated structure factors. Absorption and temperature corrections were not used, since both were considered negligible when compared with errors introduced by the intensity observation.

### Structural determination

Since there are only two MoBe<sub>12</sub> units in the body-centered cell, the molybdenum atoms must lie at 0, 0, 0 and  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ , and since Mo is so much heavier than Be we may assume that the signs of all the structure factors are positive if the structure is centrosymmetric. In the final structure, this proves to be true. It was therefore only necessary to prepare Fourier electron-density projections for the ( $hk0$ ) and ( $hhl$ ) data to determine the structure completely. The structure\* calculated from these projections is as follows:

Space group:  $I4/mmm-D_{4h}^{17}$ .

Atoms at 0, 0, 0 and  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2} +$

2 Mo in ( $a$ ) 0, 0, 0;

8 Be in ( $f$ )  $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}; \frac{3}{4}, \frac{3}{4}, \frac{1}{4}; \frac{1}{4}, \frac{3}{4}, \frac{1}{4}; \frac{3}{4}, \frac{1}{4}, \frac{1}{4}$ ;

8 Be in ( $i$ )  $X_1, 0, 0; \bar{X}_1, 0, 0; 0, \bar{X}_1, 0; 0, X_1, 0$ ;

8 Be in ( $j$ )  $X_2, \frac{1}{2}, 0; \bar{X}_2, \frac{1}{2}, 0; \frac{1}{2}, \bar{X}_2, 0; \frac{1}{2}, X_2, 0$ ;

with  $X_1 = 0.344$ ,  $X_2 = 0.284$ .

If the composition were MoBe<sub>13</sub>, the extra Be would necessarily lie at 0, 0,  $\frac{1}{2}$ , at 1.57 Å from the Be's in ( $j$ ); and no adjustment can lengthen this distance. Tables 1 and 2 give calculated and observed structure factors for ( $hk0$ ) and ( $hhl$ ) respectively. The agree-

Table 1. Calculated and observed structure factors ( $hk0$ )

$hkl$	$F_c$	$F_o$	$hkl$	$F_c$	$F_o$
110	68.5	69	730	49.2	35
220	61.2	77	840	44.9	47
330	60.5	62	950	42.6	52
440	59.7	53	10,6,0	37.2	25
550	49.5	54	600	49.9	48
660	54.6	54	710	29.6	33
770	17.5	21	820	20.6	30
880	36.5	31	930	44.2	46
990	38.5	25	10,4,0	21.8	22
200	70.2	70	11,5,0	29.1	22
310	64.3	67	800	58.9	51
420	34.2	32	910	42.6	45
530	53.4	54	10,2,0	34.3	41
640	33.4	38	11,3,0	29.6	25
750	42.5	33	12,4,0	33.2	17
860	28.0	28	10,0,0	32.0	31
970	29.8	22	11,1,0	29.6	17
400	84.8	100	13,3,0	25.3	14
510	52.3	49	12,0,0	40.9	21
620	52.7	52	14,0,0	28.7	11

\* The structure is isomorphous with that of ThMn<sub>12</sub> reported by Florio, Rundle & Snow (1952) after the original presentation of this paper at the 1951 A.C.A. meeting.

Table 2. *Calculated and observed structure factors (hkl)*

<i>hkl</i>	$F_c$	$F_o$	<i>hkl</i>	$F_c$	$F_o$
110	68.7	76	224	37.8	42
220	61.6	72	334	43.5	40
330	60.9	71	444	45.9	40
440	60.1	70	554	39.9	42
550	49.7	61	664	44.7	43
660	55.0	61	774	15.8	15
770	19.3	21	884	32.2	25
880	36.9	36	994	34.3	24
990	38.9	32	10,10,4	25.1	21
10,10,0	28.2	27	006	41.0	36
11,11,0	20.0	20.7	116	30.0	27
002	75.8	91	226	13.9	18
112	54.5	67	336	34.5	29
222	25.1	32	446	22.2	21
332	53.7	60	556	32.1	31
442	31.1	34	666	24.1	17
552	47.0	51	008	42.4	34
662	32.5	34	118	23.7	24
772	18.1	17	228	23.6	25
882	21.5	24	338	27.3	22
992	38.1	27	448	28.1	24
10,10,2	26.3	12	558	26.1	21
004	76.4	77	668	29.6	21
114	36.8	38			

ment factor  $R = \sum ||F_o| - |F_c|| \div |F_o|$  is 0.13 for (*hk*0) and 0.15 for (*hhl*).

### Twinning habit

An interesting feature of the structure is the pseudo-hexagonality of the twofold axis. This is readily apparent in the even-order Weissenberg layer-line diagrams around [100], which are strikingly similar to the even-order Weissenberg diagrams around the sixfold axis of  $\text{TiBe}_{12}$  (Raeuchle & Rundle, 1952). This pseudo-hexagonality is apparent in the atomic positions, and [100] deviates from a sixfold axis primarily in that atoms  $60^\circ$  apart around [100] may differ in their  $x$  parameters by  $\frac{1}{2}$  in a non-hexagonal manner.

It may be noted that the nearly close-packed hexagonal layers of beryllium atoms occurring in the  $\text{TiBe}_{12}$  structure perpendicular to the sixfold axis occur here also, though in a more distorted form since the layers no longer have hexagonal symmetry, perpendicular to the twofold axes. These nearly close-packed layers, in a sense, give rise to the pseudo-hexagonality.

In the course of the investigation crystals were frequently found that were twinned around [011]. That the lattice dimensions are such as to accommodate, such twinning follows from the pseudo-hexagonality mentioned before. When twinning occurs along [011], the ( $2n, k, l$ ) layer diagrams will not be changed (except for a slight doubling of spots, which can be observed only with good resolution). On the other hand, spots on the odd layer lines will not be superposed by the twinning, but will alternate along the film. Since a very large fraction of the  $\text{MoBe}_{12}$  crystals were twinned, it would have been possible to be misled by the twinned odd layers and thus choose an incorrect primitive cell.

### Discussion

The projection of the structure on to (001) is given in Fig. 1. The local atomic configuration is quite

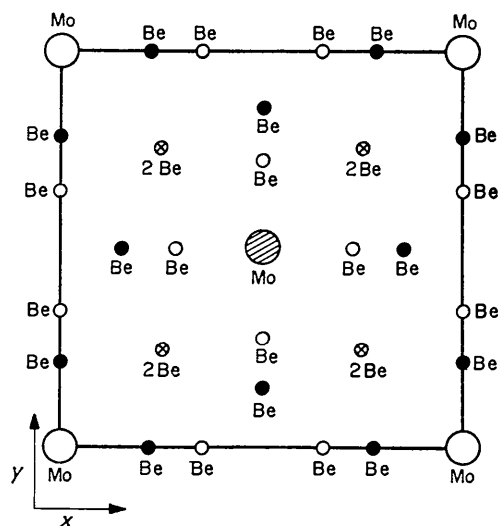


Fig. 1. Projection of the structure of  $\text{MoBe}_{12}$  on to (001). Open circles are at  $y = 0$ , solid and shaded circles at  $y = \frac{1}{2}$ , and crossed circles at  $y = \frac{1}{4}$  and  $\frac{3}{4}$ .

similar to that in the  $\text{TiBe}_{12}$  structure. As a matter of fact, this determination of the  $\text{MoBe}_{12}$  structure has furnished clues to a possible refinement in the  $\text{TiBe}_{12}$  structure. The present indication is that the refinement will increase the similarity between the two structures.

The interatomic distances occurring in the  $\text{MoBe}_{12}$  structure are listed in Table 3. The accuracy of these

Table 3. *Interatomic distances in MoBe<sub>12</sub>*

Mo	4 Be	2.50 <sub>1</sub> Å
	8 Be	2.78 <sub>0</sub>
	8 Be	2.63 <sub>8</sub>
$\text{Be}_I (\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ , etc.	2 Mo	2.78 <sub>0</sub>
	2 Be	2.11 <sub>7</sub>
	4 Be	2.21 <sub>1</sub>
	4 Be	2.11 <sub>8</sub>
$\text{Be}_{II} (0.334, 0, 0)$ etc.	1 Mo	2.50 <sub>1</sub>
	4 Be	2.21 <sub>1</sub>
	4 Be	2.65 <sub>8</sub>
	2 Be	2.35 <sub>5</sub>
	2 Be	2.31 <sub>2</sub>
	1 Be	2.26 <sub>8</sub>
$\text{Be}_{III} (0.216, 0, \frac{1}{4})$ etc.	2 Mo	2.63 <sub>8</sub>
	2 Be	2.31 <sub>2</sub>
	4 Be	2.11 <sub>8</sub>
	2 Be	2.22 <sub>1</sub>
	2 Be	2.35 <sub>5</sub>

values cannot be readily assessed from the intensity data since the moderately low value of  $R$  is obtained because the intensities depend largely on the Mo positions, which are special ones. If we assume that the accuracy of these interatomic distances is sufficient to justify a 'valence' calculation, using Pauling's

(1947, 1949) rules, we obtain the 'valences' listed in Table 4. We must emphasize that these 'valences' are

Table 4. *Calculated valences*

Mo	3.36
Be <sub>I</sub>	2.59
Be <sub>II</sub>	1.85
Be <sub>III</sub>	2.27

obtained by a purely formal treatment of data, and any decision on the merit of such valences must be left open, particularly since the validity of the Pauling approximation of single-bond radii has been questioned.\* Nevertheless, the calculated 'valences' furnish a basis for some interesting conjectures and are therefore presented here.

The calculated valences may be compared with Pauling's (1949) valences of 6 for molybdenum and 2 for beryllium. At first glance the two sets of valences do not seem to agree, but if the number of 'valence' electrons per unit cell is calculated, one finds 60.4 using the observed valences, and 60 using Pauling's valences. If this agreement is assumed not to be trivial, and if the validity of Pauling's valences be conceded, the present observations would indicate a shift of electrons from the Mo-Be bonds to Be-Be bonds. Such a shift lowers the molybdenum valence and raises that of beryllium. Pauling (1949) also points out that the single-bonded radius of a metallic element can vary with its valence state. In the calculation of the valences in Table 4, the single-bonded radii based on valences of 6 for molybdenum and 2 for beryllium have been used. This procedure would be strictly correct only if the valences calculated in Table 4 were roughly equal to the valences from which the radii were obtained. Since they are not, the valences of Table 4 cannot be considered as an accurate measure of the extent of electron shift, but only as an indication that some shift seems to have occurred.

Since the literature contains suggestions that the

\* See, for instance, Hume-Rothery & Coles (1954) concerning this point and also the direction of electron shift mentioned later.

electronic shift should occur towards the transition metal atoms (see again, Hume-Rothery & Coles (1954)), which is contrary to the present formal 'valence' calculations, further experimental work is needed to resolve the question.

*Note.*—A copy of this paper was submitted to Mr W. J. Koshuba for comment. He referred it to Mr W. B. Wilson of the X-ray diffraction and Metallography Laboratory at the Aircraft Nuclear Propulsion Department, General Electric, Cincinnati, Ohio. Mr Wilson has re-examined the X-ray data now on file at that laboratory, on which the paper by Gordon *et al.* was based. His analysis of Gordon's single-crystal films shows that the lattice constants and space group are in essential agreement with the results reported here and that odd-order lines from Gordon's larger cell must have been reported from powder diagrams where they might, in fact, be caused by a second phase (perhaps  $\text{MoBe}_2$ ).

He points out, however, that Gordon's density of 3.13 g.cm.<sup>-3</sup>, experimentally determined using Clerici-solution technique, agrees better with the formula  $\text{MoBe}_{13}$  than with  $\text{MoBe}_{12}$ . This is true but the only positions available for the two Be atoms, if the cell is to retain even tetragonal symmetry, is on the four-fold axis, and this would lead to an Mo-Be distance which at most would be  $\frac{1}{2}c_0$  or 2.167 Å, which is far too small. He further suggested that perhaps it was this consideration that led Gordon to report the primitive cell.

#### References

- BAENZIGER, N. C. & RUNDLE, R. E. (1949). *Acta Cryst.* **2**, 258.  
 FLORIO, J. V., RUNDLE, R. E. & SNOW, A. I. (1952). *Acta Cryst.* **5**, 449.  
 GORDON, S. G., MCGURTY, J. A., KLEIN, G. E. & KOSHUBA, W. J. (1951). *J. Metals*, N. Y. **3**, 637.  
 HUME-ROTHERY, W. & COLES, B. R. (1954). *Advances in Phys.* **3**, 149.  
 PAULING, L. (1947). *J. Amer. Chem. Soc.* **69**, 542.  
 PAULING, L. (1949). *Proc. Roy. Soc. A*, **196**, 343.  
 RAEUCHLE, R. F. & RUNDLE, R. E. (1952). *Acta Cryst.* **5**, 85.