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# The Crystal Structure of $WAl_{12}$, $MoAl_{12}$ and (Mn, Cr)$Al_{12}$

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The crystal structure of $WAl_{12}$ has been determined from powder samples. The unit cell is body-centred cubic and $a = 7{\cdot}580$ Å. There are two $WAl_{12}$ units per cell. The space group is $T_h^5$-$Im3$. Two W atoms are placed in special positions $0, 0, 0, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ and 24 Al atoms are in positions $24(g)$ with $y = 0{\cdot}184$ and $z = 0{\cdot}309$. The calculated density is $3{\cdot}88$ g.cm.$^{-3}$.

$MoAl_{12}$ and (Mn, Cr)$Al_{12}$ (the $G$ phase) are isomorphous with $WAl_{12}$. $a = 7{\cdot}573$ Å for $MoAl_{12}$ and $a = 7{\cdot}507$ Å for (Mn, Cr)$Al_{12}$.

## Introduction

The tungsten–aluminium system was investigated by Clark (1940), who found among others an intermetallic compound of approximate composition $WAl_{12}$. The crystal structure of this compound was, however, not worked out.

Our own preliminary work on a series of alloys indicated that the structure was of a new type. It also soon became apparent that a diffraction pattern obtained by Little & Hume-Rothery (1948) from a ternary compound Mn–Cr–Al (the $G$ phase) showed resemblance to the diffraction pattern of $WAl_{12}$.

Alloys of aluminium with molybdenum of composition $MoAl_{12}$ were also examined.

## Experimental details

Samples of tungsten–aluminium and molybdenum–aluminium alloys were prepared by powder methods. All samples contained a small amount of the $\alpha$ (aluminium) or $\delta$ (probable composition $W_2Al_9$)* phases. For this reason neither accurate density measurements nor chemical analysis could be undertaken.

Dr K. Little kindly lent to the authors the original samples of the $G$-phase alloys and also prepared by melting an alloy from which minute $WAl_{12}$ crystals and plates of the $\delta$ phase were isolated. Separation of these two components was attempted on a small scale in a Frantz isodynamic separator with some success, but complete separation was not achieved.

X-ray photographs were taken in a precision 19 cm. powder camera (Adam, 1954). Filtered copper radiation ($\lambda K\alpha_1 = 1{\cdot}54050$ Å) was used for the study of the tungsten and molybdenum alloys. Photographs of the Mn–Cr–Al alloys were taken with copper, iron and chromium radiations. Films thus obtained were measured with high precision using a new film-measuring device based on the luminous marker line principle by Lees (1952). It is claimed that these measurements are more accurate than the results published by Little & Hume-Rothery (1948).

Integrated intensity measurements were made in a standard manner using the Hilger recording microphotometer. An intensity calibration strip was exposed on each film.

In the first instance an approximate absorption factor was applied, and calculated and measured intensities of neighbouring lines only were compared in groups. An attempt was subsequently made to obtain an overall check of intensities. Various absorption factors were tried and values of log $(I_o/I_c)$ were plotted against $(\sin\theta/\lambda)^2$. A very satisfactory straight-line plot was obtained for a composite absorption factor

$$A = \alpha\tau,$$

where $\alpha$ is the absorption factor depending on $\mu R$;
$\tau$ is the micro-absorption factor (Taylor, 1945) or the particle-absorption factor (Brindley, 1945; see also de Wolff, 1951), depending on $(\mu_p-\mu)a$ tabulated by Taylor;
$\mu$ is the mean absorption coefficient of the powder;
$\mu_p$ is the absorption coefficient of the particle;
$R$ is the radius of specimen;
and $a$ is the radius of the particle.

A scale factor and temperature correction were obtained from the plot of log $(I_o/I_c)$ against $(\sin\theta/\lambda)^2$.

## The crystal structure of $WAl_{12}$

All the powder lines obtained from this alloy were indexed on the basis of a body-centred cubic lattice. The size of the unit cell obtained from the best photographs of the magnetically separated crystals was

$$a = 7{\cdot}5803 \pm 0{\cdot}0005 \text{ Å}$$

at room temperature. Samples prepared by powder methods, however, have usually smaller unit cells; in one case a value as low as $a = 7{\cdot}568(5)$ Å was found. A certain amount of line broadening was observed in this case.

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* *Note added in proof.*—Recent work by the authors suggests that $WAl_5$ is a more probable composition of the $\delta$ phase.

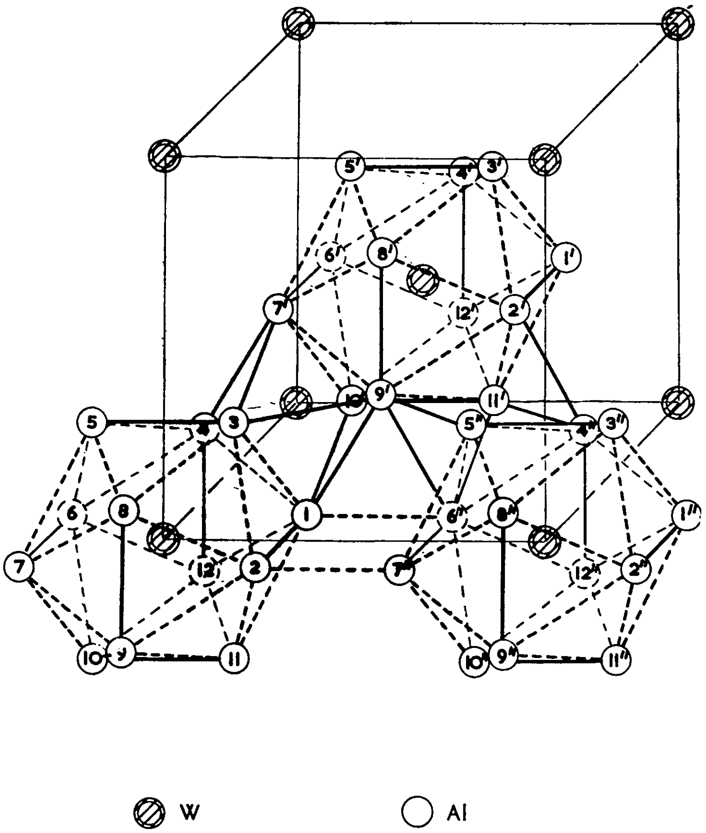

Fig. 1. The crystal structure of $WAl_{12}$.

Since neither accurate chemical analysis nor density measurements could be made on existing samples, the formula was deduced from the consideration of atomic volumes. Assuming that the atomic volumes of the constituents are not altered drastically by alloying, the most probable formula is $WAl_{12}$.

The only systematic absences observed were those characteristic of a body-centred cubic lattice. Packing considerations lead to the conclusion that the available space can be well filled if formula $WAl_{12}$ and space group $T_h^5$-$Im3$ are accepted. Each of the two tungsten atoms placed in special positions $0, 0, 0, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ would then be surrounded by twelve aluminium atoms in 24($g$) $0, y, z$, etc. (see Fig. 1). The calculated density of the alloy is 3·88 g.cm.$^{-3}$.

Algebraic expressions giving distances between various atoms in terms of $y$ and $z$ can be easily derived for the proposed structure, and a few guesses of probable values of $y$ and $z$ can be made by assuming equality of certain interatomic distances. Intensity calculations were made for six sets of likely values for $y$ and $z$ and were compared with measurements. Very good agreement between calculated and measured intensities was found (Table 1) for $y = 0{\cdot}184$, $z = 0{\cdot}309$. These parameters were obtained by assuming the distance Al(1)–Al(2) to be equal to Al(1)–Al(9′) and the distance Al(1)–Al(3) to be equal to Al(1)–Al(6″) (atoms numbered as in Fig. 1).

To test the structure the conventional reliability

Table 1. *Comparison of calculated and observed intensities for the* $WAl_{12}$ *structure*

$N = h^2+k^2+l^2$

| $N$ | $I_c$ | $I_o$ | $N$ | $I_c$ | $I_o$ |
|---|---|---|---|---|---|
| 2 | 864 | 769 | 48 | 14 | 20 |
| 4 | 126 | 133 | 50 | 263 | 248 |
| 6 | 433 | 435 | 52 | 84 | 85 |
| 8 | 42 | 48 | 54 | 124 | 121 |
| 10 | 596 | 586 | 56 | 43 | 56 |
| 12 | 282 | 287 | 58 | 34 | 38 |
| 14 | 703 | 675 | 62 | 111 | 113 |
| 16 | 103 | 100 | 64 | 2 | — |
| 18 | 146 | 148 | 66 | 156 | 167 |
| 20 | 45 | 53 | 68 | 55 | 53 |
| 22 | 34 | 38 | 70 | 227 | 224 |
| 24 | 167 | 159 | 72 | 272 | 250 |
| 26 | 316 | 323 | 74 | 332 | 333 |
| 30 | 102 | 93 | 76 | 29 | 25 |
| 32 | 35 | 42 | 78 | 167 | 172 |
| 34 | 228 | 226 | 80 | 16 | Trace |
| 36 | 146 | 140 | 82 | 98 | 95 |
| 38 | 358 | 371 | 84 | 254 | 245 |
| 40 | 27 | 41 | 86 | 420 | 402 |
| 42 | 75 | 87 | 88 | 133 | 129 |
| 44 | 25 | 38 | 90 | 503 | 571 |
| 46 | 164 | 168 | 94 | 575 | 511 |

Table 2. *The d values and indices for the G phase*

$N = h^2+k^2+l^2$

| | Little & Hume-Rothery (1948)* | | Present authors | | | | |
|---|---|---|---|---|---|---|---|
| Line | *d* (Å) | *N* | *d* (Å) | *N* | *I* | Measurement | *a* (Å) |
| 1 | 5·135 | 6 | 5·2639 | 2 | *s* | Good | 7·4443 |
| 2 | 3·007 | 18† | 3·0499 | 6 | *m*– | Good | 7·4707 |
| 3 | 2·623 | 25 | 2·6429 | 8 | *m*– | Fair | 7·4752 |
| 4 | — | — | 2·608(7) | — | *vvw* | Doubtful | — |
| 5 | 2·333 | 32 | 2·3661 | 10 | *vs* | Good | 7·4824 |
| 6 | — | — | 2·343(9) | — | *vvw* | Doubtful | — |
| 7 | 2·297 | 33 | 2·3296 | Al | *w* | Good | — |
| 8 | 2·247 | 34 | 2·226(2) | — | *vvw* | Doubtful | — |
| 9 | 2·194 | 36 | 2·1612 | 12 | *vs* | Good | 7·4866 |
| 10 | 2·135 | 38 | 2·121(8) | — | *vvw* | Doubtful | — |
| 11 | 2·093 | 40 | 2·0743 | — | *vw* | Fair | — |
| 12 | 2·065 | 41 | 2·0491 | — | *vw* | Fair | — |
| 13 | 1·978 | 45 | 2·0021 | 14+Al | *vs* | Good | 7·4912 |
| 14 | 1·854 | 51 | 1·8715 | 16 | *m* | Good | 7·4860 |
| 15 | 1·754 | 57 | 1·7652 | 18 | *m*– | Good | 7·4890 |
| 16 | 1·590 | 69 | — | — | ‡ | — | — |
| 17 | — | — | 1·6750 | 20 | *w*– | Fair | 7·4910 |
| 18 | 1·519 | 76 | 1·5293 | 24 | *m* | Good | 7·4921 |
| 19 | 1·503 | 77 | 1·4697 | 26 | *m* | Fair | 7·4941 |
| 20 | 1·411 | 88 | 1·427(8) | Al | *vw* | Doubtful | — |
| 21 | 1·364 | 94 | Poor resolution | | | Doubtful | — |
| 22 | 1·279 | 107 | 1·2856 | 34 | *vs* | Fair | 7·4964 |
| 23 | 1·260 | 110 | 1·2493 | 36 | *s* | Good | 7·4960 |
| 24 | 1·217 | 118 | — | — | ‡ | — | — |
| 25 | 1·213 | 120 | 1·2162 | 38 | *vs* | Good | 7·4973 |
| 26 | 0·896 | 219 | 0·89690 | 70 | *s* | Good | 7·5040 |
| 27 | 0·871 | 232 | 0·87232 | 74 | *s* | Good | 7·5040 |
| 28 | 0·818 | 262 | 0·81884 | 84 | *m* | Good | 7·5048 |
| 29 | 0·791 | 281 | 0·79130 | 90 | *s* | Good | 7·5069 |

* The *d* values are converted to Ångström units.
† In the original paper this value is given in error as 24.
‡ Not observed.

factor was worked out for calculated and observed intensities. The value obtained, $R = 0{\cdot}06$, can be considered very satisfactory. The errors in $y$ and $z$ are probably less than $\pm 0{\cdot}001$.

## Crystal structure of $MoAl_{12}$

Samples of this alloy gave diffraction patterns practically indistinguishable from $WAl_{12}$. The unit-cell dimension measured from photographs of alloys prepared by powder methods was found to be

$$a = 7{\cdot}573\ \text{Å}\ .$$

Intensity measurements were not attempted. Visual estimates agreed well with calculations based on the same parameters as $WAl_{12}$ and it is concluded, therefore, that the structure of $MoAl_{12}$ is essentially the same as $WAl_{12}$. The calculated density of $MoAl_{12}$ is 3·22 g.cm.$^{-3}$.

## Crystal structure of (Mn,Cr)$Al_{12}$ alloy (the *G* phase)

The existence of the *G* phase in the Mn–Al and Cr–Mn–Al systems was first reported by Little, Raynor & Hume-Rothery (1946). Little & Hume-Rothery (1948) made a further X-ray investigation of the *G* phase in the ternary system and proposed a formula $MnAl_{12}$. Their diffraction pattern fitted a primitive cubic cell with $a = 13{\cdot}25$ kX.

Marchand (1947) also examined the *G*-phase alloys and found that his diffraction pattern could be indexed on the basis of a body-centred cubic structure with $a = 7{\cdot}47$ kX. (7·48 Å). The large unit cell proposed by Little & Hume-Rothery was necessary in order to account for a number of weak reflexions occurring at fairly low angles.

In Table 2 some of the spacings measured by the authors are compared with those of Little & Hume-Rothery. Only the relevant low-angle values and three of the high-angle lines are reproduced.

Disregarding the questionable very weak lines, the main diffraction pattern of the *G* phase fits very well a body-centred cubic cell, as shown by a straight-line plot (graph not reproduced) of *a* values against the Nelson–Riley (1945) function. By extrapolation to $\theta = 90°$ we found

$$a = 7{\cdot}507\ \text{Å}\ .$$

Assuming indices proposed by Little & Hume-Rothery, and plotting *a* values against the Nelson–Riley function, the scatter greatly exceeds the error of measurements.

Attempts were made to find a larger unit which would explain the very weak lines unaccounted for by the 7·507 Å cell. A cell $a = 13·00$ Å (i.e. $7·507\times\sqrt{3}$), which is the nearest approach to the Little & Hume-Rothery value in agreement with the majority of the $d$ values, must be ruled out because a set of impossible lines would have to be explained, namely $N = 60$, 156 and 252. Doubling the unit cell to $a = 15·014$ Å would account for some of the extra lines, although on the whole the fit is not very satisfactory; it is admitted, however, that the accuracy of measurements of the very very weak lines is not sufficient to warrant the rejection of the double cell.

There is little doubt, however, that lines (Table 2) 7 and 20 and a weak shoulder to line 13 (clearly resolved when chromium radiation is used) are due to a trace of aluminium present in the samples. Photographs taken with a stationary specimen show that these lines are 'spotty' while all the other lines are perfectly smooth. The question of the remaining very weak lines cannot be positively settled on the evidence presently available, but it is the opinion of the authors that they belong to an unidentified impurity.

It is noteworthy, however, that a good agreement was obtained between calculated and visually estimated intensities assuming the same type of structure and parameters as in $WAl_{12}$. This would indicate that the structure of the (Mn, Cr)$Al_{12}$ alloy is very similar to that of $WAl_{12}$ and $MoAl_{12}$. The calculated density of the $G$ phase is 2·92 g.cm.$^{-3}$.

## Discussion

Fig. 1 illustrates the crystal structure of $WAl_{12}$, and interatomic distances are given in Table 3. Each tungsten atom is surrounded by twelve aluminium atoms. Each aluminium atom has ten aluminium neighbours, five at 2·79 Å and five at 2·88 Å. There are interstices in the structure at 0, ½, 0, etc. and ¼, ¼, ¼, etc., being 6-fold and 8-fold respectively.

Table 3. *Interatomic distances in* $WAl_{12}$, $MoAl_{12}$ *and* (Mn, Cr)$Al_{12}$

Atoms are numbered as in Fig. 1; $M$ = W, Mo or (Mn, Cr).

| | $WAl_{12}$ | $MoAl_{12}$ | (Mn, Cr)$Al_{12}$ |
|---|---|---|---|
| $M$–Al(1–12) | 2·72 Å | 2·72 Å | 2·70 Å |
| Al(1)–(2)<br>Al(1)–(9′) | 2·79 | 2·79 | 2·77 |
| Al(1)–(3)<br>Al(1)–(6″) | 2·88 | 2·88 | 2·86 |

The average Al–Al distance is 2·84 Å in the $WAl_{12}$ and $MoAl_{12}$ alloys and 2·81 Å in the $G$ phase.

Brillouin zones were examined for the $WAl_{12}$ alloy. If one accepts a valency of 3 for aluminium, the electron-to-atom ratio in the alloys examined is not less than about 2·5 even if one accepted with Raynor (1944) a negative number as representing the valency of a transition element. The first important Brillouin zone bound by {310} planes was found to be too small to accommodate the required number of electrons. This zone must therefore be full and some overlap into the next zones must exist. Volumes of further zones were found to increase in small steps, and there is no apparent reason for selecting one in preference to the others.

The crystal structures of several compounds of aluminium with transition elements of the first long period (e.g. Robinson, 1952, 1953; Nicol, 1953) have been shown to give rise to prominent first Brillouin zones which are not completely full, assuming that the transition elements absorb electrons. In addition, distances were found between the transition metal and aluminium atoms which were noticeably shorter than one could expect from the co-ordination, and this effect was associated with the possibility of electron transfer.

The absence of a first prominent Brillouin zone which can contain rather more than the postulated number of electrons, and the lack of abnormally short interatomic distances, indicate that $WAl_{12}$, $MoAl_{12}$ and (Mn, Cr)$Al_{12}$ do not belong to the class of electron compounds and no conclusions regarding the effective valencies of transition metals can be drawn from this type of alloy.

The authors wish to thank Dr K. Little for the loan of samples of $G$ phase and also for preparing some of the $WAl_{12}$ alloys, Mr J. Williams for preparing several of the $WAl_{12}$ and $MoAl_{12}$ alloys by powder methods, and Mr L. D. Muller for separation of the two phases of Al–W alloys in the Frantz separator.

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