OTT, H. (1925). *Z. Kristallogr.* **61**, 515.
RAMSDELL, L. S. (1944). *Amer. Min.* **29**, 431.
RAMSDELL, L. S. (1945). *Amer. Min.* **30**, 519.
RAMSDELL, L. S. (1947). *Amer. Min.* **32**, 64.
RAMSDELL, L. S. & KOHN, J. A. (1952). *Acta Cryst.* **5**, 215.
TOMITA, T. (1960). *J. Phys. Soc. Japan*, **15**, 99.
WILSON, A. J. C. (1942). *Proc. Roy. Soc.* A, **180**, 277.
ZHDANOV, G. S. (1945). *C. R. Acad. Sci., URSS*, **48**, 43.
ZHDANOV, G. S. & MINERVINA, Z. V. (1945). *C. R. Acad. Sci. URSS*, **48**, 182.

Acta Cryst. (1964). **17**, 57

The Structures of the Intermetallic Phases $MoAl_{12}$, $ReAl_{12}$ and $TcAl_{12}$

BY L. K. WALFORD

Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England

(*Received* 3 *April* 1963)

X-ray methods have been used to refine the structures of $MoAl_{12}$, $ReAl_{12}$ and $TcAl_{12}$. The unit cell is *b.c.c.* and the structures are nearly the same as that of WAl_{12}. The interatomic distances of the three phases are compared and those of $MoAl_{12}$ are compared with distances in other Mo–Al phases.

1. Introduction

The molybdenum–aluminum phase diagram has recently been investigated at the aluminum-rich end by Clare (1961), who reported a new phase corresponding to the formula $MoAl_7$ and confirmed that the compound richest in aluminum had the formula $MoAl_{12}$.

The phase $ReAl_{12}$ was first reported by Savitskii, Tylkina & Povarova (1961) and was later confirmed by Alte da Veiga (1962), who gave $a = 7{\cdot}5280 \pm 0{\cdot}0005$ Å.

$TcAl_{12}$ has been reported as having a *b.c.c.* unit cell with $a = 7{\cdot}5270 \pm 0{\cdot}0003$ Å (Alte da Veiga & Walford, 1963). Powder photographs of all three phases were found to be similar.

2. Material

The $MoAl_{12}$ crystal used in the refinement was picked from several given by Mr J. W. H. Clare and Dr R. S. Harding of the British Aluminium Co. Ltd., Banbury. Crystals of the other phases were prepared by Mr L. M. d'Alte da Veiga in this laboratory.

The crystals chosen were approximately 0·1 mm cubes, so only the normal scaling correction for absorption was necessary. Extinction, although presumably reduced by the use of small crystals, was still found to be present in the most intense reflexions (see § 5).

3. Unit cell and space group

The cell dimension of each phase was measured by the method of Farquhar & Lipson (1946) with unfiltered Fe radiation. The values obtained were:

$MoAl_{12}$	$7{\cdot}5815 \pm 0{\cdot}0005$ Å
$ReAl_{12}$	$7{\cdot}5270 \pm 0{\cdot}0005$
$TcAl_{12}$	$7{\cdot}5255 \pm 0{\cdot}0005$

The space group is the same as that of WAl_{12} (Adam & Rich, 1954), *viz. Im*3.

4. Density and composition

The densities of the Mo, Re and Tc phases were measured by the displacement method and found to be 3·20, 3·90 and 3·25 g.cm^{-3} respectively (all $\pm 0{\cdot}05$). The calculated densities are 3·23, 3·94 and 3·27 g.cm^{-3} respectively.

The composition of $MoAl_{12}$ has been determined by neutron activation analysis of small samples (*ca* 2 mg) of the crystals. This work was kindly undertaken by Mr H. Simpson of the Chemistry Group, Isotope Research Division, Wantage Radiation Laboratory of the United Kingdom Atomic Energy Authority (Simpson, 1964).

The samples were dissolved and irradiated with a comparator in the BEPO reactor for about 10 seconds, followed immediately by the counting of γ-radiation greater than 1·7 meV, resulting from the short lived aluminum isotopes. The molybdenum was measured by counting the 0·14 meV gamma peak due to ^{99}Tc (the decay product of ^{99}Mo) from the same samples two days later.

The results of this analysis gave

$$22{\cdot}6 \pm 0{\cdot}1 \text{ wt\% Mo}$$
$$77{\cdot}7 \pm 0{\cdot}3 \text{ wt\% Al}$$

which agrees well with the theoretical value of 22·7 wt% Mo for the formula $MoAl_{12}$. This determination corresponds to the formula $MoAl_{12\cdot2\pm0\cdot1}$.

5. Collection of intensities

Reflexions of the form (0*kl*) were collected on zero-layer normal-beam Weissenberg photographs, filtered

Mo $K\alpha$ radiation and a multiple-film technique being used. An intensity scale was made for each crystal, using a reflexion from the zone used to collect the intensity data, and intensities out to $\sin\theta/\lambda = 1{\cdot}2$ were measured. The intensities were corrected for Lorentz and polarization effects and allowance was made for absorption and resolution of the $\alpha_1\alpha_2$ doublet by scaling F_o to F_c in regions of $\sin\theta/\lambda$. Large F_o's suffering from extinction were not used in the Fourier syntheses or in the calculation of the R indices.

6. Isomorphism with WAl_{12}

Adam & Rich (1954) reported that diffraction patterns from powders of WAl_{12} and $MoAl_{12}$ were practically indistinguishable. The structure of WAl_{12} has space group $Im3$ with 2W in $2(a)$ and 24Al in $24(g)$ with $y = 0{\cdot}184$, $z = 0{\cdot}309$. Powder photographs of $ReAl_{12}$, $TcAl_{12}$ and $MoAl_{12}$ were similar, so the structure of WAl_{12} was taken as the starting point in each refinement.

7. Refinement of the [100] projection

The refinements were carried out by means of successive F_o–F_c syntheses, using the atomic scattering factors given by Forsyth & Wells (1959). After several cycles in which reflexions out to $\sin\theta/\lambda = 0{\cdot}7$ were used, the refinements were completed with the use of all the measured reflexions. The final R indices were 0·075, 0·07 and 0·06 for $MoAl_{12}$, $ReAl_{12}$ and $TcAl_{12}$ respectively.

The asymmetric unit contains one transition-metal atom, one aluminum atom and two double aluminum atoms, all of which are resolved. The final F_o and F_o–F_c syntoeses for $MoAl_{12}$ are shown in Figs. 1 and 2. The corresponding maps for the other two phases are essentially the same as those shown. The values of the parameters found were:

	y	σ_y	z	σ_z
$MoAl_{12}$	0·1854	0·0002	0·3083	0·0003
$ReAl_{12}$	0·1880	0·0002	0·3080	0·0003
$TcAl_{12}$	0·1877	0·0002	0·3083	0·0003

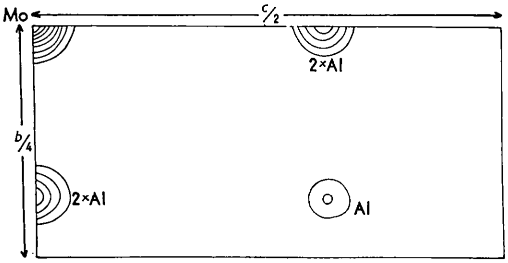

Fig. 1. Final F_o synthesis. The contours are at equal arbitrary intervals.

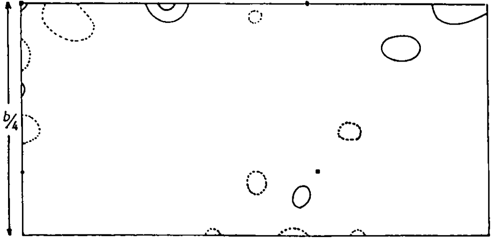

Fig. 2. Final $(F_o - F_c)$ synthesis. The contour intervals are one-eighth those of the F_o; negative contours are shown as broken lines. Squares mark the atomic sites.

The standard deviations in the coordinates were calculated in the usual way from the ratio of the r.m.s. slope on the relevant axis in the F_o–F_c map to the curvature at the atomic site in the F_o map (Lipson & Cochran, 1953, p. 308).

Discussion

The phases $MoAl_{12}$, $ReAl_{12}$ and $TcAl_{12}$ are nearly isostructural with WAl_{12}. The structure consists of two isolated, nearly regular icosahedra; aluminum atoms occupy the vertices, with a transition-metal atom at the centre of each. The two icosahedra are related by a body-centring operation.

Table 1. *Bond lengths for the three structures*

Atom	Neighbour	$MoAl_{12}$ (Å)	$ReAl_{12}$ (Å)	$TcAl_{12}$ (Å)	σ (Å)	Other neighbours
T–M	12Al	2·728	2·716	2·717	0·003	
Al	1Al	2·811	2·831	2·826	0·005	1T–M
	1Al	2·907	2·891	2·886	0·005	
	4Al	2·882	2·863	2·864	0·005	
	4Al	2·794	2·758	2·758	0·005	

Table 2. *Mean interatomic distances for the* Mo–Al *system*

Bond	$MoAl_{12}$	$MoAl_5$	$MoAl_4$	Mo_3Al_8	Mo_3Al
Mo–Al	2·73 Å	2·79* Å	2·70 Å	2·76 Å	2·77 Å
Al–Al	2·84	2·79*	2·90	2·79	

* These distances are calculated on the assumption that $MoAl_5$ is exactly isostructural with WAl_5 (Adam & Rich, 1955).

The interatomic distances are given in Table 1 and the mean bond lengths for $MoAl_{12}$ and other Mo–Al phases are compared in Table 2. No other structures in the Tc–Al and Re–Al systems have been refined, so comparisons of bond lengths in these systems cannot be made at present.

Clare's (1961) chemical analysis gave the ratio of molybdenum to aluminum in α(MoAl) as 1 : 13. He suggested two possible explanations: either there is a composition range due to the replacement of the molybdenum atoms by aluminum atoms or there is a vacancy instead of a molybdenum atom in some unit cells.

No evidence for either of these suggestions has been found in the present work. The structure refinement, density measurement and chemical composition all indicate that the 'molecule' is not $MoAl_{13}$ but $MoAl_{12}$.

In all three structures the transition-metal to aluminum distance is significantly shorter than the inter-aluminum distance, which suggests that the strongest interaction is between aluminum and transition-metal atoms. This shortening of these bonds is more marked in $MoAl_{12}$ than in the other Mo–Al phases, with the exception of $MoAl_4$ (Leake, private communication), but is not so marked as in the phases of aluminum with transition metals of the first long period (Taylor, 1954).

I should like to thank Prof. Sir Nevill Mott, F.R.S. and Dr W. H. Taylor for provision of facilities and for their interest and encouragement. I am indebted to Dr M. V. Wilkes and Mr E. N. Mutch for providing time on the EDSAC II computer. The technetium was kindly lent by Dr G. T. Rogers, A.E.R.E., Wantage. I also wish to thank the D.S.I.R. for the award of a Research Studentship.

References

Adam, J. & Rich, J. B. (1954). *Acta Cryst.* **7**, 813.

Adam, J. & Rich, J. B. (1955). *Acta Cryst.* **8**, 349.

Alte da Veiga, L. M. d' (1962). *Phil. Mag.* Series 8, **7**, 1247.

Alte da Veiga, L. M. d' & Walford, L. K. (1963). *Phil. Mag.* Series 8, **8**, 349.

Clare, J. W. H. (1961). *J. Inst. Metals*, **89**, 232.

Farquhar, M. C. M. & Lipson, H. (1946). *Proc. Phys. Soc.* **58**, 200.

Forsyth, J. B. & Wells, M. (1959). *Acta Cryst.* **12**, 412.

Lipson, H. & Cochran, W. (1953). *The Crystalline State*, Vol. III. London: Bell.

Savitskii, E. M., Tylkina, M. A. & Povarova, K. B. (1961). *Zh. Neorg. Khim.* **8**, 1962.

Simpson, H. (1964). *Acta Cryst.* **17**, 59.

Taylor, W. H. (1954). *Acta Met.* **2**, 684.

Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.*

Acta Cryst. (1964). **17**, 59

The empirical formulae of intermetallic compounds by neutron activation.

By H. Simpson, *Wantage Research Laboratories (A.E.R.E.), Wantage, Berkshire, England*

(*Received* 3 *April* 1963)

Neutron activation analysis has been applied to the determination of the empirical formulae of some technetium–aluminum and molybdenum–aluminum compounds. An outline of the technique is given, as this method is of general application and is particularly suitable when accurate results are required from limited quantities (*ca.* 5 mg) of material.

In neutron activation analysis (see *e.g.* Jenkins & Smales, 1956), the sample for analysis is irradiated with neutrons together with a known standard of the element to be determined. The induced activities for each constituent element can be characterized by the natures and energies of emitted radiations and their half-lives. When the measured radioactivity is of short half-life, it is usual for the analysis to be non-destructive, using some form of γ-ray spectrometry.

Several advantages are offered:

(i) It is highly sensitive, which means that only small quantities of material are required. Satisfactory results can be obtained with one milligram or less.

(ii) It is specific for the element determined, provided that elementary precautions are taken to ensure measurement of radioactivity which is characteristic of that element. Gamma-ray spectrometry and half-life determinations are often sufficient for this.

(iii) Where the activity is short-lived, repeat analyses can be carried out on the same sample to improve precision.

When the specimen contains nuclides which absorb neutrons strongly, errors can arise if the distributions of these elements in the specimen and sample differ. This is because the full neutron flux is unable to reach the inner regions of the solid sample. This source of error can usually be overcome by dispersing the material in a medium with a low neutron cross-section (*e.g.* in aqueous solution). The method is then destructive to the sample, but repeated measurements can still be made on the solution, if the half-lives are suitable.

Examples of analyses

Some doubt about the true composition of the intermetallic compound '$MoAl_{12}$' has resulted from the conventional chemical analyses reported by Clare (1960). These analyses indicate a deficiency of molybdenum and an average composition corresponding to $MoAl_{13}$, although