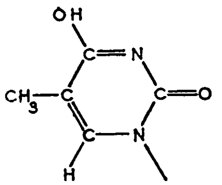
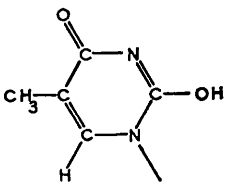
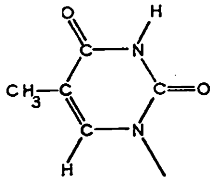


(1)



(3)



(2)

La molécule ne porte que deux atomes d'hydrogène capables de former des liaisons hydrogène, à savoir l'hydrogène porté par O_3' et l'hydrogène labile du cycle hexagonal.

L'hydrogène porté par O_3' ne peut servir que dans les liaisons O_3'–O_6 (2,7 Å) pour la forme *A*, et O_3'–O_2 (2,8 Å) pour la forme *B*, les autres distances d'approche étant supérieures ou égales à 3,3 Å. Cette disposition sans ambiguité d'une part, l'alignement spatial presque parfait d'autre part des atomes $C_4N_1O_3'$ rendent probable la liaison hydrogène N_1–O_3' pour les deux formes, ce qui donnerait à *A* et *B* la même formule tautomère (2).

Les deux formes *A* et *B* ne différeraient donc que par une symétrie, en passant de l'une à l'autre, de liaison hydrogène par rapport à la droite $C_4N_1O_3'$, formes probablement très voisines du point de vue énergétique, ce qui expliquerait assez bien la cristallisation simultanée, ou quasi simultanée, des deux formes cristallines.

Nous tenons à exprimer ici, notre reconnaissance à Sir Lawrence Bragg qui a bien voulu suivre ce travail, au Docteur Taylor pour ses bienveillants conseils au cours de cette étude et au Docteur Cochran qui nous a constamment guidé et a effectué pour nous certains calculs sur la machine EDSAC; nous remercions également le Mathematical Laboratory pour l'aide qu'il nous a apportée au cours de nos calculs.

Notre gratitude va aussi au British Council qui nous a permis de poursuivre cette étude à l'Université de Cambridge où la majeure partie de ce travail a été accomplie.

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The Structure of α(V–Al)

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The most aluminium-rich compound in the V–Al system has been shown to be isomorphous with $Mg_3Cr_2Al_{18}$. Accurate values for the atomic parameters have been determined. The interatomic distances and some special features of the structure are discussed.

1. Introduction

The V–Al system was investigated by Carlson, Kenney & Wilhelm (1955). They found three peritectic phases α, β and γ at the aluminium-rich end of the phase diagram. The most aluminium-rich of these phases, α, was shown to be cubic with $a = 14{\cdot}586$ Å and to have space group *Fd3m*; it was given the formula VAl_{11}.

2. Material

The crystals used in the present work were kindly given to the Laboratory by Dr A. D. I. Nicol, for whom they were made by Dr D. W. Wakeman. They were extracted electrolytically from a slowly-cooled ingot containing about 3% wt. vanadium. The extracted crystals were of two kinds, one of which proved to be the α phase of Carlson *et al.* These crystallized as octahedra; the other crystals, monoclinic plates having formula unit approximately VAl_7, do not correspond to any of the phases found by Carlson *et al.*

Several analyses of the cubic α crystals were obtained. The results differed rather widely, probably because of the very small quantity of vanadium in the samples. The analysis for which the largest quantity of material was available, and which should therefore be the most reliable, was kindly made by Aluminium Laboratories Ltd, of Banbury. They found the sample to contain 15·35% wt. vanadium and 84·6% wt. aluminium, which makes the formula unit VAl_{10}. As will be seen, this analysis agrees with the density and proposed structure of the α phase.

3. Unit cell

The density of the crystals, determined by both flotation and displacement methods, was $2{\cdot}79 \pm 0{\cdot}05$ g.cm.$^{-3}$. The lattice parameter a was found by the method of Farquhar & Lipson (1946) to be $14{\cdot}492 \pm 0{\cdot}004$ Å for the crystal used in the structure analysis. The mass of the contents of the unit cell is 5120 ± 100 a.m.u., so that if the chemical analysis is correct there are 16V and 160Al atoms per cell (5236 a.m.u.).

Laue and oscillation photographs confirmed the space group *Fd*3*m* found by Carlson *et al.*

4. Determination of the structure

A complete rotation photograph of α(VAl) about [001] was almost identical with a similar photograph of the compound $Mg_3Cr_2Al_{18}$, the structure of which has been given by Samson (1954). This compound has a = 14·55 Å and the atoms are arranged in space group *Fd*3*m* as follows:

Al	in	$96(g)$	x, x, z .
Al	in	$48(f)$	$x^1, 0, 0$.
Mg	in	$16(d)$	$\frac{5}{8}, \frac{5}{8}, \frac{5}{8}$.
Mg	in	$8(b)$	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$.
Cr	in	$16(c)$	$\frac{1}{8}, \frac{1}{8}, \frac{1}{8}$.

$$x = 0{\cdot}067, \quad z = 0{\cdot}298, \quad x^1 = 0{\cdot}134 .$$

All the parameters in this structure can be obtained from a [110] projection (Fig. 1) in which most of the atoms are resolved.

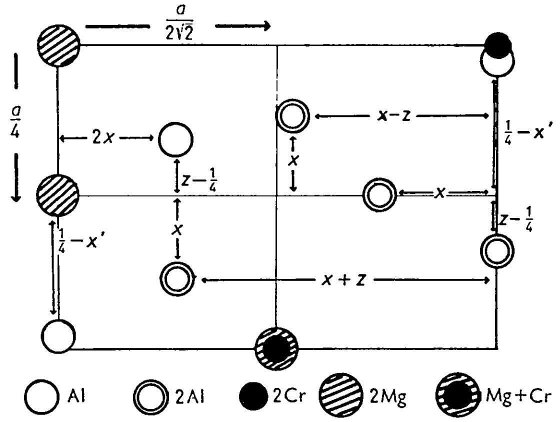

Fig. 1. The asymmetric unit of the [110] projection of $Mg_3Cr_2Al_{18}$.

Reflexions from the [011] zone were collected on a zero-layer Weissenberg photograph from an octahedral crystal with an edge of 0·03 mm.; filtered Mo $K\alpha$ radiation and a pack of four films were used. The intensities of reflexions, which could be seen out to $(\sin\theta)/\lambda \sim 0{\cdot}8$, were measured by visual comparison with an intensity scale made with the same crystal. A correction was made for the Lorentz and polarization factors; but not for absorption or extinction. Allowance was made for resolution of the $\alpha_1\alpha_2$ doublet by scaling F_o to F_c in regions of $(\sin\theta)/\lambda$ in the usual way.

The observed structure amplitudes showed fair agreement with those calculated for the $Mg_3Cr_2Al_{18}$ structure with vanadium in place of chromium, and aluminium in place of magnesium. Accurate parameters were found by the use of F_o and (F_o-F_c) Fourier projections. This structure contains 168 Al atoms per cell; such a composition is not incompatible with the density and chemical analysis, but in the course of the refinement it became clear that the $8(b)$ sites were not occupied in the crystal used. The final arrangement of atoms was:

Al_1	in	$96(g)$	x, x, z .
Al_2	in	$48(f)$	$x^1, 0, 0$.
Al_3	in	$16(d)$	$\frac{5}{8}, \frac{5}{8}, \frac{5}{8}$.
V	in	$16(c)$	$\frac{1}{8}, \frac{1}{8}, \frac{1}{8}$.

$$x = 0{\cdot}0654, \quad z = 0{\cdot}3009, \quad x^1 = 0{\cdot}1407 .$$

The agreement index R was 11%. The final F_o and (F_o-F_c) syntheses are shown in Fig. 2. The final

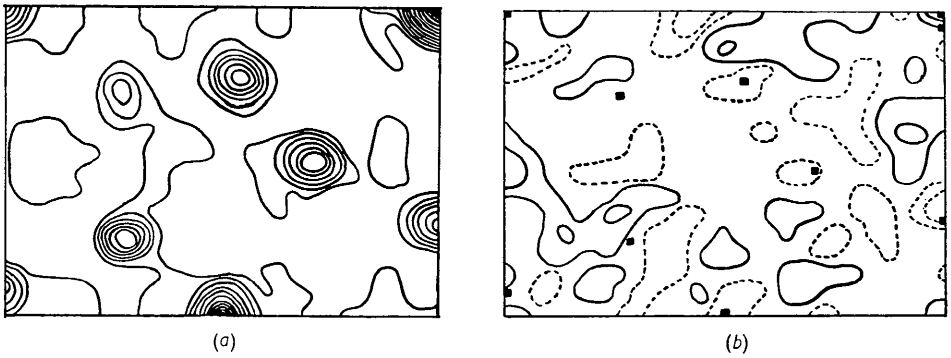
(a) (b)

Fig. 2. Final F_o and (F_o-F_c) [110] Fourier projections. (a) F_o. The contours are at arbitrary intervals. (b) (F_o-F_c). The contour intervals are one-fifth those of the F_o; negative contours are shown as broken lines. Squares represent atomic sites.

$(F_o - F_c)$ synthesis has a peak at the $8(b)$ position equal to about one-tenth of the aluminium peak height. This may mean that the $8(b)$ position is 10% occupied by aluminium; on the other hand this peak is no higher than others occurring elsewhere in the $(F_o - F_c)$ synthesis and may be caused by errors in the observed intensities.

5. Description of the structure

Each vanadium atom is surrounded by six Al_1 and six Al_2 neighbours in a nearly regular icosahedron. The icosahedra are linked together in the [110] direction, sharing Al_2 atoms. Fig. 3(*a*) shows a group of four icosahedra linked in this way. Fig. 3(*b*) illustrates how four of these groups are arranged in the unit cell to form a tetrahedral framework. The Al_3 atoms occupy the mid-points of the faces of the tetrahedron, and the empty $8(b)$ position is at its centre.

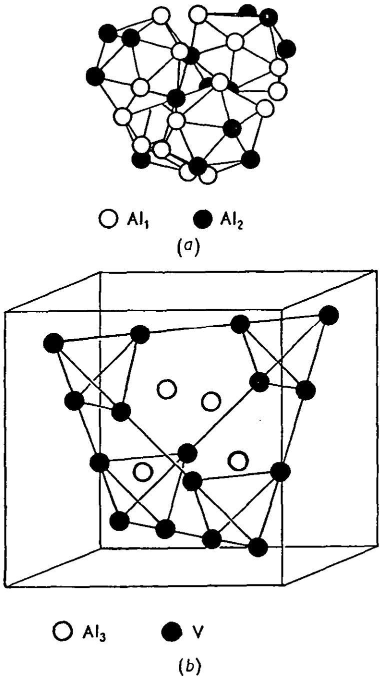

Fig. 3. The structure of α(V–Al). (*a*) The V atoms are at the centres of the icosahedra, which are drawn as though solid. (*b*) The Al atoms in contact with V are omitted.

6. Interatomic distances

The interatomic distances are listed in Table 1. Of the twelve neighbours of any one V atom six are at a distance of 2·57 Å, which is considerably shorter than the sum of the 12-coordinated radii for vanadium and aluminium (2·77 Å). Similar contractions have been found in other aluminium-rich transition-metal compounds and are thought possibly to be associated with electron transfer to the transition metal atom (Taylor, 1954). There is no direct evidence for this in α(V–Al), both because of the uncertainty in composition and because no absolute measurements of the diffracted X-ray intensity have been made. The mean distance between Al atoms which are in contact with V atoms is 2·80 Å, which is about normal for this type of compound. The Al_3 atom, which has no V neighbours, has $12Al_1$ neighbours at 3·08 Å.

Table 1. *Interatomic distances*

		Distance (Å)	σ (Å)
V	$6Al_1$	2·826	0·004
	$6Al_2$	2·572	0·002
Al_3	$12Al_1$	3·083	0·003
Al_1	$2Al_1$	2·943	0·007
	$2Al_1$	2·740	0·010
	$1Al_1$	2·679	0·010
	$2Al_2$	2·880	0·004
	$1Al_2$	2·679	0·005
	$2Al_3$	3·083	0·003
	1V	2·826	0·004
Al_2	$4Al_2$	2·882	0·005
	$2Al_1$	2·679	0·005
	$4Al_1$	2·880	0·004
	2V	2·572	0·002
Hole	$12Al_1$	3·181	0·004
	$3Al_3$	3·137	0·001

7. Discussion

A striking feature of this structure is the large average atomic volume, 17 Å^3 per atom, compared with 15·1 for Co_2Al_9, 15·5 for $MnAl_6$ and 16·4 for pure aluminium. This high atomic volume is due to loose packing of atoms in positions which are not in contact with V atoms. It is therefore probable that it is a strong Al–V interaction, giving rise to the framework of linked icosahedra, which is important in the formation of this structure. Al atoms in sites not in contact with V can take little part in this interaction and are either dropped out, or show an abnormally large radius.

I am indebted to Dr A. D. I. Nicol for kindly providing the crystals and for taking the original photographs; to Dr M. G. Bown who recognized the similarity to ε(MgCrAl)–$Mg_3Cr_2Al_{18}$; and to the Aluminium Laboratories Ltd for the chemical analysis. I should like to thank Prof. N. F. Mott, and Dr W. H. Taylor for provision of facilities and for their interest and encouragement. I am particularly grateful to Dr P. J. Black for much helpful advice. For financial support I must thank the Ministry of Supply and Newnham College, Cambridge.

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