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The Structure of the Intermetallic Phase α′(VAl)

By P. J. Brown

Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England

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The structure of the monoclinic α′-phase in the vanadium–aluminium system has been determined and refined. This phase has the ideal composition V_7Al_{45} and is structurally related to both the α and β vanadium–aluminium phases. A description of the structure is given, and the interatomic distances are discussed and compared with those found in the other two phases.

1. Introduction

A recent investigation of the vanadium–aluminium alloy system (Bailey, Carlson & Smith, 1958) has shown that there exist five intermediate phases, α-VAl_{10}, α′-VAl_7, β-V_4Al_{23}, γ-VAl_3 and δ-V_5Al_8. The δ phase has the γ-brass structure and that of the γ-phase is isomorphous with $TiAl_3$ (Brauer, 1943). The structure of the β-phase has been determined by Smith & Ray (1957) and independently by the present author (Brown, 1957*a*). The structure of the α-phase has been shown to be closely similar to that of ε(MgCrAl) (Brown, 1957*b*).

The three phases in this system which are most rich in aluminium belong to the group of complex aluminium-rich alloys in which considerable interest has centred in recent years (Raynor, 1949; Taylor, 1954); and the two whose structures were already known had shown some interesting systematic trends in the orientation of the abnormally short V–Al bonds (Brown, 1957*a*). The analysis of the structure of the phase VAl_7 was undertaken both to complete the structural investigation of the phase diagram and to provide further evidence to test the trends noticed previously.

2. Material

The crystals used in the analysis were extracted electrolytically from an alloy containing 2·5% weight vanadium. The materials used for its preparation were a vanadium–aluminium master alloy containing about 20% weight vanadium which was kindly made up by the Aluminium Research Laboratories, Banbury, and 'super-purity' aluminium supplied by the British Aluminium Company. The alloy was cooled from 800 °C. to 675 °C. at the rate of 1 °C./min. and then rapidly quenched from this temperature. The extracted crystals were mainly plates of the α′ phase but a few α crystals were also found. The α′ crystals were often multiply twinned and X-ray examination showed that the twin axis was normal to (100), the plane of the plates.

3. The unit cell

Laue, oscillation and Weissenberg photographs taken of the α′ crystals showed that the unit cell was monoclinic and enabled approximate values of the lattice parameters to be calculated. More precise values were determined using the θ-method described by Weisz, Cochran & Cole (1948); the film strip used by these workers to detect the X-rays was replaced in the present case by a Geiger counter used in conjunction with a linear ratemeter. The values found were:

$$\begin{aligned} a &= 25\cdot604 \pm 0\cdot014 \text{ Å} \\ b &= 7\cdot6213 \pm 0\cdot0018 \\ c &= 11\cdot081 \pm 0\cdot012 \\ \beta &= 128^\circ\ 55' \pm 2'. \end{aligned}$$

The volume of the unit cell is 1680 ± 2 Å^3 and the density of the crystals, measured by a flotation method, is 3·10 ± 0·03 g.cm.$^{-3}$. The mass of the contents of the unit cell is therefore 3130 ± 30 a.m.u.

A chemical analysis of 35 mg. of the crystals carried out by Messrs Johnson Matthey & Co. Ltd. gave 22·0% weight vanadium and 77·9% weight aluminium or one vanadium atom to 6·7 aluminium atoms. The mass of the unit $VAl_{6\cdot7}$ is 232 a.m.u.; there are therefore 14 vanadium atoms per cell (714 a.m.u.), the remaining 2416 a.m.u. correspond approximately to 90 aluminium atoms.

4. The space group

The Laue symmetry of the crystals as shown by X-ray photographs is $2/m$ and the systematically absent reflexions show that the unit cell is C-face centred. The possible space groups are therefore $C2$, Cm and $C2/m$. Of these the first has a centre of symmetry in the [010] projection. The second has no centre of symmetry in either the [010] or [001] projections; only in the space group $C2/m$ are both of these projections centrosymmetric.

A Wilson statistical test was applied to the intensities measured for both the [010] and [001] zones; the results obtained are shown in Fig. 1. The points for both projections lie on or above the curve for a

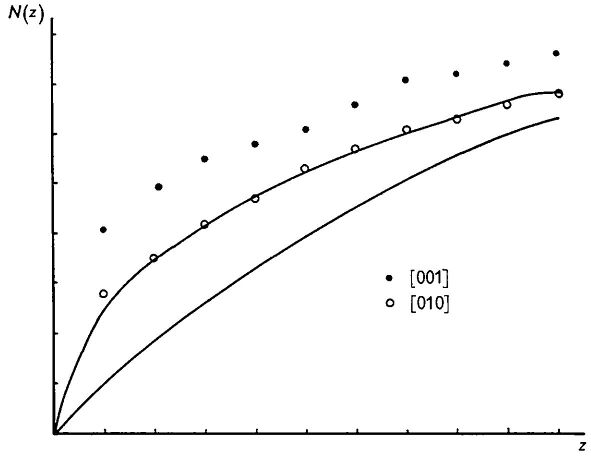

Fig. 1. Tests for centrosymmetry of the [001] and [010] projections of α'(V–Al).

centric distribution. The holosymmetric space group $C2/m$ was therefore chosen, and during the refinement of the structure no evidence was found to contradict this choice.

5. Collection of intensities

The crystal used for the collection of intensity data was a small block, cut from one of the twinned plates so as to contain one component only, approximately cubic in shape and with edges about 0·05 mm. in length. For this size of crystal the correction of the intensities for absorption of Mo $K\alpha$ radiation can be assumed to be a function of $\sin\theta/\lambda$ only, within the accuracy of the measurements.

Reflexions from this crystal of the form $h0l$ were recorded on a zero-layer, normal-beam Weissenberg photograph with Mo $K\alpha$ radiation. A multiple-film technique was used, and intensities out to $\sin\theta/\lambda = 1{\cdot}0$ were measured by visual comparison with an intensity scale made using a reflexion from the same crystal. About 400 non-zero intensities were included in this range; they were corrected for the Lorentz and polarization effects. Absorption and the effect of increasing resolution of the $\alpha_1\alpha_2$ doublet were taken into account by the method of scaling. Initially the possibility of extinction was ignored but in the final stages of the refinement it was found necessary to make a rough correction for it.

Reflexions of the form $hk0$ were collected in a similar way; finally the $hk1$ and $hk2$ reflexions were recorded on two equi-inclination Weissenberg photographs and their intensities measured since it was found that these data were necessary to complete the refinement of the structure.

6. The [001] Patterson projection

The [001] Patterson projection was calculated and is shown in Fig. 2. The weight of the origin peak is 534 and the structure is to contain 14 vanadium and approximately 90 aluminium atoms; therefore if the weight of the peak corresponding to an Al–Al vector is α^2 and that of a V–V vector is $4\alpha^2$ then, assuming that there is no overlap of atoms in projection, $\alpha^2 = 3{\cdot}7$. The y-axis of the unit cell is only 7·6 Å in length so that in the space group $C2/m$ there are mirror planes perpendicular to y at distances 3·8 Å apart. Atoms in general positions in the structure must lie at least 1·3 Å from these planes. The peak A in the Patterson projection at distance 2·7 Å from the origin along the y axis is the sum of peaks corresponding to vectors between each atom in a general position and the atom to which it is related by reflexion in the mirror-plane. The weight of this peak is 158 which leads to the conclusion that either there are about 80 aluminium atoms in general positions and all the vanadium atoms are in special positions, or else there are 8 vanadium atoms and about 48 aluminium atoms in general positions. As there are only about 90 aluminium atoms in the structure the second combination seemed more reasonable and it was decided to proceed on the assumption that the vanadium atoms occupy one set of 2(a), one set of 4(i), and one set of 8(j) positions, and that the aluminium atoms occupy at least 6 sets of 8(j) and 8 sets of 4(i) positions.

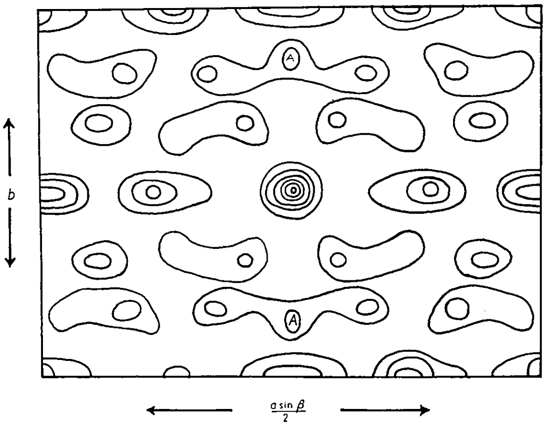

Fig. 2. [001] projection of the Patterson function.

7. The [010] Patterson projection

The similarity between the b axis of α'(V–Al) and the a axis of β(V–Al), each of which is about 7·6 Å in length and is intersected by mirror planes, suggested that the vanadium atoms in 8(j) positions might be surrounded by a complex such as that illustrated in Fig. 3(a) which is similar to that around the V_2 atoms in the β-structure. Such a complex when viewed in projection down the [010] axis (Fig. 3(b)) will show a peak corresponding to the superposition of one aluminium and two vanadium atoms, surrounded by a ring of ten approximately evenly spaced peaks at a distance of about 2·2 Å from the central peak; alternate peaks correspond to single and double aluminium atoms.

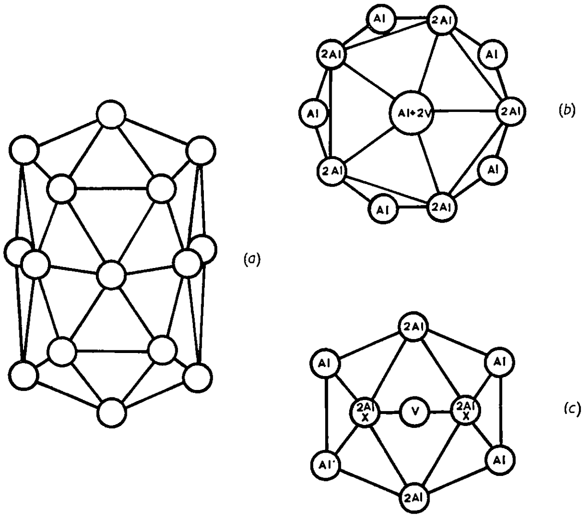

Fig. 3. Coordination polyhedra in the structure of α′(V–Al).

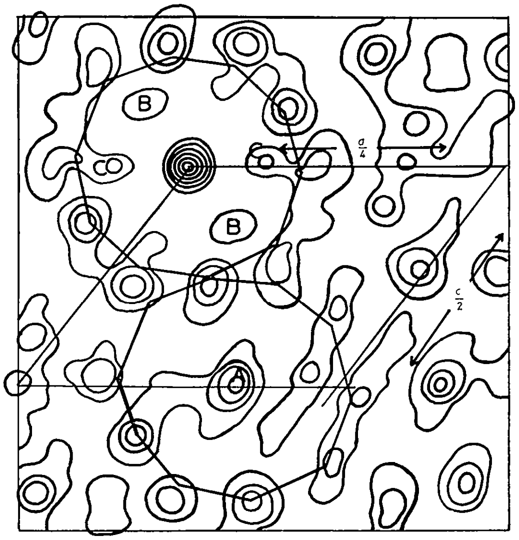

Fig. 4. [010] projection of the Patterson function.

The [010] Patterson projection is shown in Fig. 4. The highest peak apart from the origin peak is that marked *A* and was associated with the vector between two of the complexes referred to in the previous paragraph. The ten-fold rings surrounding both this peak and the origin peak have been outlined. The other vanadium atoms in the structure lie on the mirror plane and evidence from the structures of both α and β V–Al suggests that these vanadium atoms will be 12-coordinated by aluminium atoms at the corners of a nearly regular icosahedron. If this is so the icosahedra must be orientated so that one of their mirror planes lies in the mirror plane of the structure and when viewed in projection down [010] it will appear as in Fig. 3(*c*). The vector V–*X* in this projection can be associated with either of the peaks *B* and *C* in the [010] Patterson projection. The peak *C* has twice the weight of peak *B* and was therefore associated with the vanadium atoms in 4(*i*) positions, the weaker peaks *B* being associated with the atoms in 2(*a*) positions, and in this way the orientation of the icosahedra around these vanadium atoms was determined. Using this information it was then possible to postulate a structure which was in fairly good agreement with both [010] and [001] Patterson projections. The positions of atoms in this structure are given in Table 1; *x* and *z* coordinates for the atoms Al_8, Al_9, Al_{10} and Al_{17} could not be fixed with any certainty from the Patterson projections.

8. Refinement of the [010] projection

The atoms of the structure proposed in the previous section are resolved in the [010] projection except for

Table 1. *Atomic coordinates in the structure of* α′ V–Al

Type of atom				Initial coordinates			Final coordinates		
2 V_0	in	2(*a*)	(0, 0, 0)						
4 V_1	in	4(*i*)	$(x_1, 0, z_1)$	0·25		0·25	0·2514 ± 0·0003		0·2628 ± 0·0007
8 V_2	in	8(*j*)	(x_2, y_2, z_2)	0·08	0·312	0·74	0·0857 ± 0·0002	0·3270 ± 0·0005	0·7530 ± 0·0005
2 Al_0	in	2(*d*)	$(0, \frac{1}{2}, \frac{1}{2})$						
4 Al_3	in	4(*i*)	$(x_3, 0, z_3)$	0·61		0·00	0·6164 ± 0·0005		0·0030 ± 0·0012
4 Al_4	in	4(*i*)	$(x_4, 0, z_4)$	0·28		0·06	0·2935 ± 0·0005		0·0760 ± 0·0012
4 Al_5	in	4(*i*)	$(x_5, 0, z_5)$	0·38		0·38	0·3755 ± 0·0005		0·3870 ± 0·0012
4 Al_6	in	4(*i*)	$(x_6, 0, z_6)$	0·53		0·27	0·5205 ± 0·0005		0·2840 ± 0·0012
4 Al_7	in	4(*i*)	$(x_7, 0, z_7)$	0·08		0·74	0·0815 ± 0·0008		0·7200 ± 0·0020
4 Al_8	in	4(*i*)	$(x_8, 0, z_8)$				0·1287 ± 0·0005		0·1435 ± 0·0012
4 Al_9	in	4(*i*)	$(x_9, 0, z_9)$				0·0905 ± 0·0005		0·3370 ± 0·0012
4 Al_{10}	in	4(*i*)	$(x_{10}, 0, z_{10})$				0·2255 ± 0·0005		0·4600 ± 0·0012
8 Al_{11}	in	8(*j*)	(x_{11}, y_{11}, z_{11})	0·17	0·188	0·00	0·1810 ± 0·0003	0·1830 ± 0·0008	0·0090 ± 0·0007
8 Al_{12}	in	8(*j*)	(x_{12}, y_{12}, z_{12})	0·06	0·312	0·12	0·0680 ± 0·0003	0·3180 ± 0·0008	0·1475 ± 0·0007
8 Al_{13}	in	8(*j*)	(x_{13}, y_{13}, z_{13})	0·96	0·188	0·13	0·9644 ± 0·0003	0·1800 ± 0·0008	0·1365 ± 0·0007
8 Al_{14}	in	8(*j*)	(x_{14}, y_{14}, z_{14})	0·30	0·312	0·23	0·3098 ± 0·0003	0·3180 ± 0·0008	0·2415 ± 0·0007
8 Al_{15}	in	8(*j*)	(x_{15}, y_{15}, z_{15})	0·05	0·188	0·47	0·0452 ± 0·0003	0·1940 ± 0·0008	0·4670 ± 0·0007
8 Al_{16}	in	8(*j*)	(x_{16}, y_{16}, z_{16})	0·16	0·312	0·50	0·1648 ± 0·0003	0·3070 ± 0·0008	0·4750 ± 0·0007
8 Al_{17}	in	8(*j*)	(x_{17}, y_{17}, z_{17})		0·312		0·2058 ± 0·0003	0·3140 ± 0·0008	0·2780 ± 0·0007

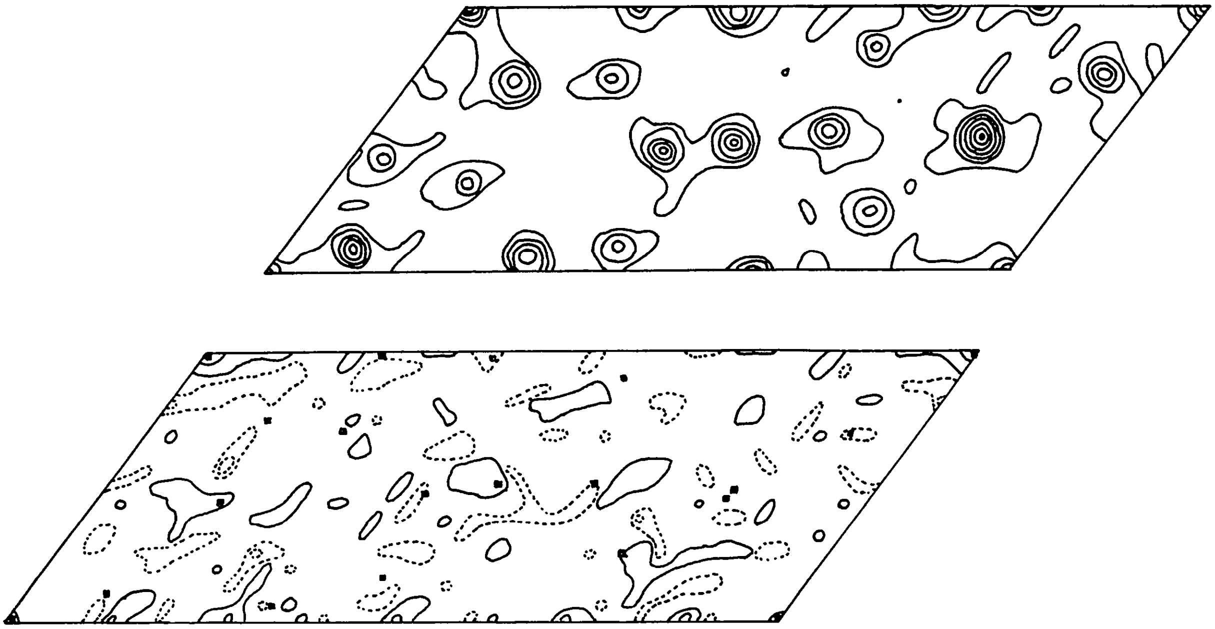

Fig. 5. Final F_o and F_o-F_c [010] Fourier projections; contours are at equal arbitrary intervals, the interval in the F_o-F_c synthesis is one fifth of that in the F_o. Negative contours are shown as broken lines. Squares mark the atomic sites.

the V_2 and Al_7 atoms which lie on top of one another. Using the coordinates determined from the Patterson projections, the structure factors out to $\sin\theta/\lambda=0{\cdot}5$ were calculated and compared with the observed structure amplitudes; a fair agreement was found. After scaling F_o to F_c in regions of $\sin\theta/\lambda$ the agreement index R was 0·45. Both the F_o and the F_o-F_c syntheses were now calculated omitting those terms whose signs were particularly uncertain. The atoms Al_8, Al_9, Al_{10} and Al_{17} appeared as positive peaks on these syntheses in positions very near to those expected on geometrical grounds; coordinates were assigned to these atoms as follows:

$x_8=0{\cdot}120$	$z_8=0{\cdot}147$
$x_9=0{\cdot}072$	$z_9=0{\cdot}270$
$x_{10}=0{\cdot}226$	$z_{10}=0{\cdot}420$
$x_{17}=0{\cdot}208$	$z_{17}=0{\cdot}270$

and a few small changes were made in the coordinates of the other atoms. The structure factors calculated using these coordinates were in considerably better agreement than formerly, and after scaling R was 0·33 which was taken to show that the structure was now substantially correct.

The x and z coordinates were refined in the [010] projection using F_o-F_c syntheses. The final R-factor over the 380 measured reflexions was 0·102. The final F_o and F_o-F_c syntheses are shown in Fig. 5; the final coordinates are given in Table 1.

9. Refinement of the [001] projection

The y-coordinates of the eight sets of atoms in general positions have to be determined from the [001] pro-

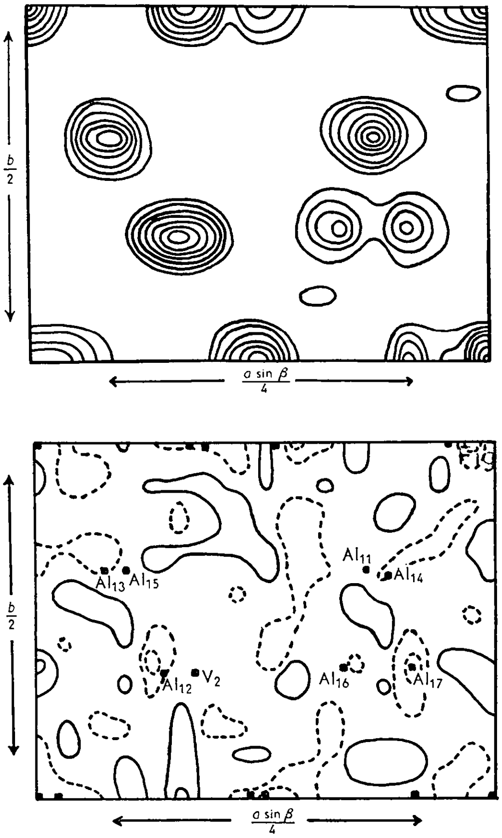

Fig. 6. Final F_o and F_o-F_c [001] Fourier projections; contours are at equal arbitrary intervals, the interval in the F_o-F_c synthesis is one fifth of that in the F_o. Negative contours are shown as broken lines. Squares mark the atomic sites.

jection. These atoms are, however, not very well resolved in this projection and occur in four groups of two, V_2, Al_{12}; Al_{11}, Al_{14}; Al_{13}, Al_{15}; Al_{16}, Al_{17} (see Fig. 6). The y coordinates of these atoms cannot therefore be determined very accurately from this projection using the zero layer data only. A few cycles of refinement were, however, carried out using F_o-F_c syntheses and the R-factor was reduced from 0·34 to 0·154. Further refinement of the coordinates in this projection was carried out using data from two non-zero layers.

In space group $C/2m$ the structure factors are of the form

$$\begin{aligned} F(hkl) &= \sum_n f_n \cos 2\pi(hx+lz) \cos 2\pi ky \\ &= \sum_n f_n \{\cos 2\pi hx \cos 2\pi ky \cos 2\pi lz - \sin 2\pi hx \\ &\qquad \times \cos 2\pi ky \sin 2\pi lz\} \end{aligned}$$

The contribution of a particular atom to the reflexion (hkl) is:

$$f_n (\cos 2\pi hx \cos 2\pi ky \cos 2\pi lz - \sin 2\pi hx \cos 2\pi ky \sin 2\pi lz)$$

and the contribution of the same atom to the reflexion $(\bar{h}kl)$ is

$$f_n (\cos 2\pi hx \cos 2\pi ky \cos 2\pi lz + \sin 2\pi hx \cos 2\pi ky \sin 2\pi lz);$$

its contribution to the sum $F(hkl)+F(\bar{h}kl)$ is therefore $2f_n (\cos 2\pi hx \cos 2\pi ky \cos 2\pi lz)$. The Fourier synthesis

$$\Psi(xy) = \sum_h \sum_k [F(hkl)+F(\bar{h}kl)] \cos 2\pi(hx+ky)$$

for a constant value of l will have peaks at the atomic positions of the [001] projection of weight proportional to $f_n \cos 2\pi lz$. The values of $\cos 2\pi lz$ for the eight

Table 2. *Contributions of the atoms in general positions to the first and second layers of the* [001] *projection*

Atom	1st layer	2nd layer
V_2	0·031	−0·995
Al_{11}	0·998	0·996
Al_{12}	0·588	−0·279
Al_{13}	0·661	−0·125
Al_{14}	0·063	−0·992
Al_{15}	−0·976	0·905
Al_{16}	−0·988	0·951
Al_{17}	−0·187	−0·930

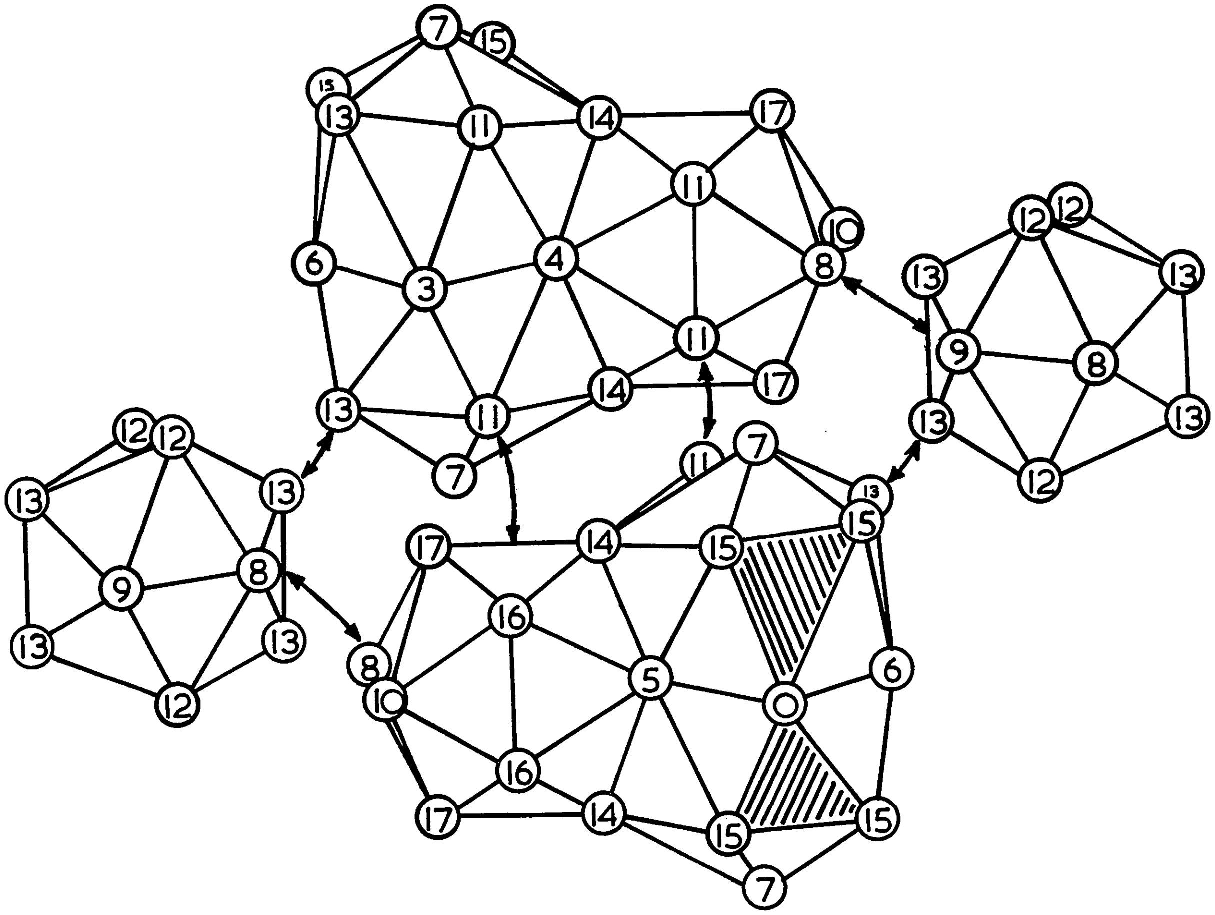

Fig. 7. Schematic diagram showing the structural units of α′(V–Al). The numbers refer to those of the Al atoms in Table 1.

atoms in general positions when l is equal to 1 and to 2 are listed in Table 2. It can be seen that V_2, Al_{14} and Al_{17} make only a small contribution to the synthesis calculated using data from the first layer, and that Al_{12} and Al_{13} make only a small contribution to that calculated using data from the second layer. Thus by using $F_o - F_c$ syntheses for the zero, first and second layers of the [001] projection it was possible to refine all the y-coordinates. The final coordinates are given in Table 1 and the agreement between F_o and F_c was as follows:

Zero layer	100 reflexions measured	$R = 0{\cdot}096$
1st layer	230 reflexions measured	$R = 0{\cdot}094$
2nd layer	200 reflexions measured	$R = 0{\cdot}095$

The final F_o and $F_o - F_c$ syntheses for the zero layer are shown in Fig. 6. The standard deviations of the atomic coordinates have been calculated from the final $F_o - F_c$ syntheses in the manner suggested by Lipson & Cochran (1953). Tabulated values of F_o and F_c are available.

10. Description of the structure

The structure of α'V–Al is most readily described in terms of the coordination polyhedra around the vanadium atoms. The polyhedra around the V_0 atoms are nearly regular icosahedra, and those around the V_1 atoms are slightly distorted icosahedra; each pair of V_2 atoms which are in contact form the nucleus of the two interpenetrating icosahedra shown in Fig. 3(a). Each of these complexes shares one pair of adjacent faces with a pair of faces of one of the V_1 icosahedra and thus form the large groups of atoms indicated schematically in Fig. 7 in their appropriate orientations. The atoms Al_{11} are shared between the two groups which have been drawn, and each of those groups shares an Al_8 and an Al_{13} atom, with one of the icosahedra around the V_0 atoms which are also shown. The structural unit thus formed extends in a thick layer by operation of the centres of symmetry at the positions of V_0 and Al_0. This causes adjacent units to share the two faces which are shaded in Fig. 6. These thick layers are stacked one above the other sharing the atoms Al_7.

11. The interatomic distances

Table 3 is a list of interatomic distances with their standard deviations. The mean Al–Al distance is 2·85 Å which is about normal for this type of compound. The main interest lies in the Al–V distances, a histogram of these distances suggests that they are divided into two groups the mean Al–V distance in the first group being 2·56 Å and the mean distance in the second being 2·79 Å. The value 2·56 Å found for the first group is significantly shorter than the sum of the twelve-coordinated radii for vanadium and aluminium (2.77 Å) whereas the mean in the second group is not very

Table 3. *Interatomic distances in the structure of* α'V–Al

Atom	Neighbours at distances given elsewhere in table	Other neighbours	Distance (Å)	Standard deviations (Å)
V_0	—	2 Al_8	2·603	0·013
		2 Al_9	2·898	0·013
		2 Al_{12}	2·825	0·007
		4 Al_{13}	2·596	0·008
V_1	—	1 Al_4	2·874	0·015
		1 Al_5	2·544	0·015
		1 Al_8	2·525	0·015
		1 Al_{10}	2·654	0·015
		2 Al_{11}	2·590	0·014
		2 Al_{14}	2·936	0·009
		2 Al_{16}	2·710	0·014
		2 Al_{17}	2·713	0·009
V_2	—	1 V_2	2·636	0·008
		1 Al_0	2·579	0·005
		1 Al_3	2·698	0·012
		1 Al_4	2·739	0·012
		1 Al_5	2·660	0·012
		1 Al_6	2·809	0·012
		1 Al_7	2·510	0·005
		1 Al_{11}	2·544	0·009
		1 Al_{13}	2·526	0·009
		1 Al_{14}	2·855	0·009
		1 Al_{15}	2·828	0·009
		1 Al_{15}	2·810	0·009
Al_0	4 V_2	2 Al_5	2·587	0·013
		2 Al_6	2·755	0·013
		2 Al_{15}	2·728	0·007
Al_3	2 V_2	1 Al_4	2·939	0·018
		1 Al_6	2·887	0·018
		2 Al_{11}	2·904	0·009
		2 Al_{12}	2·920	0·014
		2 Al_{13}	2·929	0·009
		2 Al_{17}	2·781	0·014
Al_4	2 V_2, 1 Al_3	1 Al_5	2·675	0·018
	1 V_1	2 Al_{11}	2·814	0·009
		2 Al_{11}	2·845	0·014
		2 Al_{14}	2·904	0·009
		2 Al_{14}	3·092	0·014
Al_5	1 V_1, 2 V_2	1 Al_6	2·852	0·018
	1 Al_0, 1 Al_4	2 Al_{14}	2·805	0·009
		2 Al_{15}	2·834	0·009
		2 Al_{16}	2·749	0·014
Al_6	2 V_2, 1 Al_0	2 Al_{12}	2·830	0·014
	1 Al_3, 1 Al_5	2 Al_{13}	2·778	0·009
		2 Al_{15}	2·886	0·009
		2 Al_{16}	3·229	0·014
Al_7	2 V_2	2 Al_{11}	2·898	0·019
		2 Al_{13}	2·854	0·019
		2 Al_{14}	2·886	0·019
		2 Al_{15}	2·760	0·019
		2 Al_{15}	2·919	0·019
Al_8	1 V_0, 1 V_1	1 Al_9	2·863	0·018
		1 Al_{10}	2·734	0·018
		2 Al_{11}	2·911	0·014
		2 Al_{12}	2·894	0·009
		2 Al_{13}	2·803	0·014
		2 Al_{17}	2·851	0·009
Al_9	1 V_0, 1 Al_8	1 Al_{10}	2·804	0·018
		2 Al_{12}	3·014	0·009
		2 Al_{13}	2·862	0·014
		2 Al_{15}	2·777	0·014
		2 Al_{16}	2·785	0·009
Al_{10}	1 V_1, 1 Al_8, 1 Al_9	2 Al_{16}	2·831	0·014
		2 Al_{16}	2·870	0·009
		2 Al_{17}	2·662	0·014
		2 Al_{17}	2·960	0·009
Al_{11}	1 V_1, 1 V_2, 1 Al_3	1 Al_{11}	2·788	0·012
	1 Al_4, 1 Al_4	1 Al_{13}	2·981	0·011
	1 Al_7, 1 Al_8	1 Al_{14}	2·926	0·011

Table 3 (*cont.*)

Atom	Neighbours at distances given elsewhere in table	Other neighbours	Distance (Å)	Standard deviations (Å)
Al_{11}	—	1 Al_{14}	2·805	0·010
		1 Al_{17}	2·810	0·010
Al_{12}	1 V_0, 1 Al_3, 1 Al_6 1 Al_8, 1 Al_9	1 Al_{12}	2·773	0·012
		1 Al_{12}	2·907	0·016
		1 Al_{13}	2·783	0·010
		1 Al_{13}	2·899	0·010
		1 Al_{16}	2·823	0·011
		1 Al_{17}	2·845	0·011
Al_{13}	1 V_0, 1 V_2, 1 Al_3 1 Al_6, 1 Al_7, 1 Al_8 1 Al_9, 1 Al_{11}, 1 Al_{12} 1 Al_{12}	1 Al_{13}	2·742	0·012
		1 Al_{15}	2·854	0·011
Al_{14}	1 V_1, 1 V_2, 1 Al_4 1 Al_4, 1 Al_5, 1 Al_7 1 Al_{11}, 1 Al_{11}	1 Al_{14}	2·733	0·012
		1 Al_{15}	3·013	0·011
		1 Al_{16}	2·938	0·010
		1 Al_{17}	2·940	0·011
Al_{15}	1 V_2, 1 V_2, 1 Al_0 1 Al_5, 1 Al_6, 1 Al_7 1 Al_7, 1 Al_9, 1 Al_{13} 1 Al_{14}	1 Al_{15}	2·956	0·012
		1 Al_{15}	2·833	0·016
		1 Al_{16}	3·128	0·010
Al_{16}	1 V_1, 1 Al_5, 1 Al_6 1 Al_9, 1 Al_{10}	1 Al_{16}	2·941	0·012
		1 Al_{17}	2·960	0·011
Al_{16}	—	1 Al_{17}	2·807	0·010
Al_{17}	1 V_1, 1 Al_3, 1 Al_8 1 Al_{10}, 1 Al_{10}, 1 Al_{11} 1 Al_{12}, 1 Al_{14}, 1 Al_{16} 1 Al_{16}	1 Al_{17}	2·834	0·012

different from this. These may be compared with the values 2·57 and 2·83 Å found for the two crystallographically different V–Al distances in α(V–Al) (Brown, 1957*a*) and with the mean values 2·58 and 2·80 Å for the two similar groups of distances in β(V–Al) (Smith & Ray, 1957). In all three compounds it is found that the short V–Al vectors are those which link the coordination polyhedra together. In almost all cases each aluminium atom which is in short contact with one vanadium atom is also in short contact with a second. In Table 4 are collected all the distances in the structures of α, β and α′(V–Al) between aluminium atoms which are in contact with just two vanadium atoms. The angle at the aluminium atom between the two V–Al bonds is also given. Inspection of Table 3 shows that in all cases where the mean Al–V distance belongs to the short group the angle between the bonds is close to 180°.

Table 4. *Interatomic distances and interbond angles for aluminium atoms in contact with two vanadium atoms in vanadium–aluminium alloy phases*

Compound	d_1	d_2	Angle
α-VAl	2·57 Å	2·57 Å	169·8°
α′-VAl	2·70	2·70	58·4
	2·81	2·81	56·1
	2·51	2·51	165·8
	2·60	2·52	175·8
	2·53	2·60	171·6
	2·94	2·86	91·6
	2·83	2·81	92·9
β-VAl	2·53	2·53	170·4
	2·59	2·59	168·9
	2·78	2·78	57·0

Black (1955) has pointed out a tendency for the transition-metal to aluminium distance in this type of compound to increase with the number of transition metal neighbours of the aluminium atom. In these vanadium–aluminium compounds the mean V–Al distance for aluminium atoms in contact with one vanadium atom is 2·80 Å, for those in contact with two vanadium atoms is 2·64 Å, and for those in contact with three it is 2·66 Å. This shows that in these compounds at least the strongest interaction occurs when an aluminium atom is in contact with just two vanadium atoms.

One other feature worthy of note is the distance 2·636 Å between the V_2 atoms; this is very similar to the distance (2·648 Å) between the V_2 atoms in β-VAl and is not significantly different from the closest distance of approach between atoms in pure vanadium which suggests that it exists here in much the same state as in the pure metal.

12. Summary

The structures of all the intermediate phases in the vanadium–aluminium system have now been determined. The three most rich in aluminium are intimately related to one another and have structures which are markedly different from that of VAl_3. In all three structures the vanadium atoms are coordinated by twelve other atoms which lie at the vertices of nearly regular icosahedra. These icosahedra may interpenetrate one another so that one or two of the atoms in contact with a vanadium atom are themselves vanadium atoms; otherwise the icosahedra are linked together by shared faces or corners.

The vanadium–aluminium distances in the three compounds fall into two groups and those in one of the groups are all significantly shorter than the sum of the twelve coordinated radii. It is natural to associate these two groups with a strong and a weaker V–Al interaction. The fact that the strong vanadium–aluminium bonds are those associated with V–Al–V bond angles which are all near to 180° suggests that the strong interaction in these compounds has more directional character than is usually associated with a purely metallic bond.

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Zur Kenntnis der Kristallstruktur von Lorandit, $TlAsS_2$

Von Anna Zemann und J. Zemann

Mineralogisch-Kristallographisches Institut der Universität, Göttingen, Lotzestrasse 16–18, *Deutschland*

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The crystal structure of lorandite, $TlAsS_2$, has been solved in principle from ($h0l$) and ($hk0$) X-ray-data. The essential features are screwed $As^{[3]}S_2$-chains parallel [010], which are bound together by irregularly coordinated Tl-atoms. The final R-values are: $R_{[010]} = 0{\cdot}10_0$; $R_{[001]} = 0{\cdot}17_6$.

Einleitung

Während über Thioantimonite schon eine grössere Anzahl von Strukturuntersuchungen vorliegt, ist über Thioarsenite noch verhältnismässig wenig gearbeitet worden. An erster Stelle ist zu nennen die Strukturbestimmung von Arsenfahlerz, $(Cu, Fe)_{12}(AsS_3)_4S_{0-1}$ (Machatschki, 1928; Pauling & Neumann, 1934). Für die AsS_3-Gruppe wurde dabei eine trigonal-pyramidale Gestalt mit As–S = 2,21 Å und ∢S–As–S = 103° gefunden. Diese AsS_3-Gruppe ist seitdem noch in einigen anderen Thioarseniten gefunden worden.

Es ist zu erwarten, dass Thioarsenite mit einem S:As-Verhältnis kleiner als 3:1 begrenzte oder unbegrenzte As_xS_y-Verbände enthalten, in welchen AsS_3-Pyramiden über die Schwefel zu grösseren Einheiten verknüpft sind. Tatsächlich ist Auripigment, As_2S_3, nach diesem Prinzip aufgebaut, wobei die AsS_3-Gruppen über alle Schwefelatome zu Schichten ${}^2_\infty[As^{[3]}_2S_3]$ verbunden sind (Ito, 1950). Realgar, As_4S_4, nimmt eine gewisse Sonderstellung ein (Ito, Morimoto & Sadanaga, 1952). Dieses Arsensulfid enthält $[As_4S_4]$-Moleküle, in welchen jedes As zwar pyramidal von drei nächsten Nachbarn umgeben ist; von diesen sind jedoch nur zwei Schwefel (As–S = 2,35 Å), ein Nachbar ist ein Arsen (As–As = 2,59 Å). Die vorliegende Arbeit soll einen Beitrag zur Kristallchemie der kondensierten Thioarsenite bilden, indem unseres Wissens erstmalig ein Thioarsenit vom Formeltyp $MeAsS_2$ behandelt wird.

Gitterkonstanten und Raumgruppe

Als Arbeitsmaterial standen mehrere Lorandit-Kristalle vom Fundort Allchar, Mazedonien, zur Verfügung. Die Zelldimensionen von Hofmann (1933*a*) konnten aus den Weissenberg- und Precession-Aufnahmen im wesentlichen bestätigt werden. Wir schlossen uns jedoch der Aufstellung nach 'Dana's System of Mineralogy' (1944) an. Die Gitterkonstanten der monoklinen Zelle sind:

$$a = 12{,}27,\quad b = 11{,}33,\quad c = 6{,}11\ \text{Å};\quad \beta = 104{,}2°.$$

Nach den systematischen Auslöschungen ($hk0$ nur mit $h = 2n$, $0k0$ nur mit $k = 2n$) ist die Raumgruppe $P2_1/a$–C^5_{2h}. Die Elementarzelle enthält 8 Formeleinheiten $TlAsS_2$.

Gang der Strukturbestimmung

Als sehr schwierig erwies sich die Herstellung von Präparaten zum Sammeln quantitativer Intensitäten. Die ausgezeichnete Spaltbarkeit nach mehreren ($h0l$)-Flächen gekoppelt mit einer sehr leichten plastischen Deformierbarkeit machten jedes Abschleifen unmöglich. Mangels gut geeigneter Ätzmittel führte auch die chemische Behandlung grösserer Spaltstücke nicht viel weiter. Die Daten wurden schliesslich von einem nach [010] gestreckten Spaltpräparat von ca. 20 μ Durchmesser und ca. 60 μ Länge gesammelt. Es wurden Serien von Aufnahmen mit multiplen Belichtungszeiten um [010] (Weissenberg-Äquatoraufnahmen, Cu-Strlg.) und [001] (Precession-Aufnahmen, Äquator,

Tabelle 1. *Parameter*

Atomart	Punktlage	x	y	z
Tl (1)	4(g)	0,051	0,313	0,160
Tl (2)	4(g)	0,101	0,056	0,732
As (1)	4(g)	0,190	0,820	0,237
As (2)	4(g)	0,151	0,585	0,554
S (1)	4(g)	0,125	0,320	0,750
S (2)	4(g)	0,150	0,580	0,200
S (3)	4(g)	0,125	0,790	0,510
S (4)	4(g)	0,200	0,030	0,200