Acta Cryst. (1957). **10**, 604

Composition variation in the α-phase compound of the vanadium–aluminum system.[*]

By A. E. Ray and J. F. Smith, *Institute for Atomic Research and Department of Chemistry, Iowa State College, Ames, Iowa, U.S.A.*

(*Received* 31 *May* 1957)

The structure of the α-phase compound in the vanadium–aluminum system has recently been determined by Miss Brown (1957). This structure has the space-group symmetry O_h^7–$Fd3m$ and has vanadium atoms in the 16(*c*) positions and aluminum atoms in the 96(*g*), 48(*f*), and 16(*d*) positions. An interesting feature is the large volume available at the 8(*b*) positions in the structure. Brown's data indicated that the crystals from which she obtained intensity data had 10% or less of the 8(*b*) sites occupied by aluminum atoms. The present work corroborates Brown's structure determination in detail, but the crystals investigated at this laboratory were found to have ~ 50% aluminum occupancy of the 8(*b*) sites. Thus comparison of the two sets of data indicates that the α-phase can exist over a range of composition and that the composition variation arises from the degree of occupancy of the 8(*b*) sites. Composition limits of VAl_{10} and V_2Al_{21} may be inferred.

Crystals of the α-phase compound were prepared by holding a vanadium–aluminum alloy (6 wt.% vanadium) at 665±3° C.[†] for two weeks under a helium atmosphere. The alloy was then quenched in oil, cleaned, and the aluminum matrix dissolved in 1*N*HCl. Suitable crystals were manually separated from the residue. Symmetry was confirmed by layer-line patterns taken with Weissenberg and precession cameras. Intensity data were taken with a G.–M. tube attached to a Weissenberg camera; and Cu *Kα* radiation was employed. The intensities for equivalent reflections agreed within 5% after corrections were made for Lorentz and polarization factors. The data were processed on an IBM–650 computing machine using the Least-Squares II program written by Dr M. E. Senko

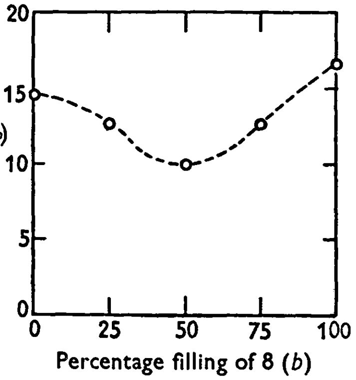

Fig. 1.

Table 1. *Magnitudes of observed and calculated structure factors for* α(Al–V)

hkℓ	$\|F_o\|$	$\|F_c\|$	hkℓ	$\|F_o\|$	$\|F_c\|$	hkℓ	$\|F_o\|$	$\|F_c\|$	hkℓ	$\|F_o\|$	$\|F_c\|$
(000)	-	158.2	5,11,1	6.0	5.8	10,10,2	9.2	9.7	6,14,4	<2.0	3.0
220	3.5	4.6	5,13,1	7.1	7.1	10,12,2	<2.1	0.8	6,16,4	4.9	5.0
260	18.7	19.4	5,15,1	<1.9	0.7	10,14,2	19.3	18.3	884	11.2	9.6
2,10,0	12.7	11.6	5,17,1	3.8	6.0	12,12,2	4.7	3.1	8,10,4	4.2	3.8
2,14,0	11.8	11.2	771	<1.7	0.8	12,14,2	<2.1	0.7	8,12,4	10.6	11.3
2,18,0	6.8	5.5	791	7.1	6.2	333	<2.2	0.6	8,14,4	2.7	2.9
400	11.8	11.4	7,11,1	3.0	3.7	353	24.9	33.6	10,10,4	12.1	10.0
440	18.6	19.6	7,13,1	6.1	5.0	373	10.3	9.2	10,12,4	13.0	10.5
480	15.4	15.3	7,15,1	19.7	19.5	393	13.9	15.3	10,14,4	4.4	2.9
4,12,0	17.7	15.6	991	9.1	9.9	3,11,3	26.8	33.2	12,12,4	20.3	16.4
4,16,0	11.3	9.4	9,11,1	8.3	7.6	3,13,3	<2.2	1.8	555	15.8	15.8
660	18.3	18.5	9,13,1	<1.9	0.2	3,15,3	<2.0	0.9	575	7.8	7.3
6,10,0	<2.4	1.0	9,15,1	9.6	9.5	3,17,3	<1.9	2.2	595	15.5	14.4
6,14,0	10.4	8.1	11,11,1	<1.9	0.3	553	2.7	2.2	5,11,5	18.9	18.3
800	< 1.7	0.3	11,13,1	2.7	3.4	573	11.1	10.6	5,13,5	<2.0	2.1
880	47.0	66.5	222	9.5	10.2	593	7.1	7.5	5,15,5	7.8	7.2
8,12,0	3.4	0.4	242	5.3	6.4	5,11,3	<2.2	0.4	775	4.3	4.7
8,16,0	2.7	1.8	262	28.4	40.9	5,13,3	11.4	9.3	795	2.5	2.2
10,10,0	13.4	11.0	282	14.7	15.0	5,15,3	<1.9	1.7	7,11,5	3.5	2.8
10,14,0	8.9	6.1	2,10,2	24.3	27.4	5,17,3	7.9	8.2	7,13,5	14.7	14.4
12,0,0	9.1	10.4	2,12,2	10.2	9.1	773	<2.0	0.1	7,15,5	<1.9	1.0
12,12,0	11.0	12.0	2,14,2	4.0	3.9	793	3.8	3.3	995	5.1	6.5
111	9.6	12.9	2,16,2	8.4	8.7	7,11,3	<2.2	1.3	9,11,5	7.6	7.5
131	6.9	5.4	2,18,2	6.4	6.6	7,13,3	<2.1	2.5	9,13,5	13.9	12.9
151	<1.7	1.6	442	13.8	13.8	7,15,3	<2.0	0.7	9,15,5	<1.9	0.7
171	20.3	25.3	462	5.3	5.4	993	9.0	8.2	11,11,5	20.5	21.0
191	5.5	5.6	482	5.5	5.7	9,11,3	2.5	1.6	11,13,5	2.7	2.7
1,11,1	<1.9	1.2	4,10,2	13.7	13.5	9,13,3	9.2	8.1	666	27.4	33.9
1,13,1	<2.1	0.3	4,12,2	7.3	6.5	9,15,3	5.8	4.9	686	13.2	13.5
1,15,1	<1.9	0.9	4,14,2	< 2.2	2.4	11,11,3	<2.0	2.3	6,10,6	24.1	26.2
1,17,1	8.5	6.8	4,16,2	6.1	5.9	11,13,3	14.2	11.7	6,12,6	<2.0	0.4
331	6.3	7.2	662	4.9	3.1	444	33.3	43.5	6,14,6	4.4	2.5
351	13.7	15.6	682	4.3	4.1	464	4.9	5.1	6,16,6	2.7	2.5
371	<1.5	0.2	6,10,2	5.6	6.1	484	14.0	13.0	886	<2.2	1.0
391	5.2	5.8	6,12,2	6.6	7.2	4,10,4	18.4	18.3	8,10,6	9.2	9.7
3,11,1	8.7	8.6	6,14,2	23.2	22.9	4,12,4	26.1	25.6	8,12,6	2.8	3.4
3,13,1	13.1	13.2	6,16,2	7.4	6.8	4,14,4	2.7	2.1	8,14,6	13.7	13.1
3,15,1	<1.9	1.6	882	<2.1	1.1	4,16,4	4.6	4.8	10,10,6	19.1	18.5
3,17,1	5.6	5.9	8,10,2	9.7	10.2	664	5.7	5.7	10,12,6	7.1	6.3
551	17.6	19.7	8,12,2	4.8	3.7	684	4.9	5.2	10,14,6	3.8	3.2
571	<1.8	1.7	8,14,2	8.6	7.9	6,10,4	4.2	3.3	12,12,6	<1.9	1.0
591	3.4	3.0	8,16,2	<1.6	1.2	6,12,4	<2.3	1.7			

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[*] Contribution No. 535. Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission.

[†] Heating the same alloy at 673° C. produced crystals having monoclinic symmetry.

of the I.B.M. Research Center, Poughkeepsie, N.Y. This program refines both the structure parameters and the temperature factors for each set of atoms. Refinement of the structure was done with the 8(b) positions 0%, 25%, 50%, 75%, and 100% occupied. Fig. 1 shows a plot of the reliability factor, $R = \Sigma||F_o|-|F_c||\div\Sigma|F_o|$, obtained from the calculations. The most intense reflection, (880), was omitted when computing R to avoid scaling errors. The magnitudes of F_o and F_c are shown in Table 1; the tabulated F_c is based on the structure with 8(b) sites 50% occupied. There is excellent agreement between the three structure parameters obtained by the least-squares refinement and those obtained by Brown:

Position	Brown	These data (8(b), 50% occupied)
96(g) (x, x, z)	$x = 0{\cdot}0654$	$x = 0{\cdot}0644$
	$z = 0{\cdot}3009$	$z = 0{\cdot}3009$
48(f) (x, 0, 0)	$x = 0{\cdot}1407$	$x = 0{\cdot}1408$

A lattice parameter of 14·516 Å was obtained from data taken on a back-reflection Weissenberg camera; Brown obtained 14·492 Å. The difference in the two values is in the direction which might be expected from the indicated difference in aluminum content.

The temperature factors are related to the vibrational amplitudes and hence to the strength of the bonds. The temperature-factor values are consistent with the bond strengths indicated by interatomic distances given by Brown. The values (Table 2) show that the vanadium atoms are most localized owing to their greater mass and strong bonding. Similarly, the aluminum atoms in the 96(g) and 48(f) sets, which are coordinated to vanadium, are more localized than the aluminum atoms in the 16(d) and 8(b) sets, which are not bonded directly to vanadium. Finally, the aluminum atoms in 8(b) with no bonds shorter than 3·1 Å have the most vibrational freedom and hence the lowest bond energy, and these are the atoms which do not seem necessary for stability of the structure.

Table 2. *Temperature factors*

Set	Temperature factor
16(c) (V)	0·12 Å
96(g) (Al)	0·52
48(f) (Al)	0·39
16(d) (Al)	1·35
8(b) (Al, 50%)	1·53

Since the crystals used in this investigation and those used by Brown were all grown on the aluminum-rich side of the compound, the difference in composition quite probably indicates a slope in the phase boundary as a function of temperature.

Reference

Brown, P. J. (1957). *Acta Cryst.* **10**, 133.

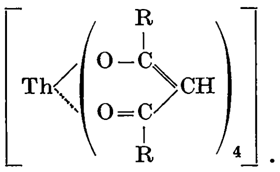
Acta Cryst. (1957). **10**, 605

Kristalldaten von Thorium-tetrakis-(dibenzoylmethan) und den isomorphen Komplexen des vierwertigen Cers und Urans.

Von Leopold Wolf und Hartmut Bärnighausen, *Institut für anorganische Chemie der Karl-Marx-Universität, Leipzig, Deutschland*

(*Eingegangen am* 12. *Juli* 1957)

Angeregt durch präparative Arbeiten auf dem Gebiet der inneren Komplexe des Thoriums mit β-Diketonen (Wolf & Jahn, 1955) interessierten wir uns für den räumlichen Bau der Verbindungen des Typs



Mit Dibenzoylmethan als Ligand gelang uns nach anfänglichen Schwierigkeiten die Röntgenstrukturanalyse bis zur Raumgruppe. Für die weitere Strukturaufklärung ist die Isomorphie des Thoriumkomplexes mit Cer-tetrakis-(dibenzoylmethan) — dargestellt von Sacconi & Ercoli (1949) — wertvoll. Das bisher in reiner Form lediglich von Albers, Deutsch, Krastinat & Osten (1952) erhaltene Urantetrakis-(dibenzoylmethan) ist ebenfalls dem Thoriumkomplex isomorph.

Zu Röntgenuntersuchungen geeignete Einkristalle der drei genannten Verbindungen wurden durch langsames Abkühlen von in der Hitze mässig konzentrierten Xylol-Lösungen erhalten. Die langen, tafeligen Kristalle gehören dem äusseren Habitus nach zur rhombisch-bipyramidalen Kristallklasse (D_{2h}–mmm) mit den Begrenzungsflächen {010}, {110}, {012}. Nach Gitterkonstantenbestimmungen aus Drehkristallaufnahmen und der rechnerischen Indizierung von Schwenkaufnahmen wurden genaue Gitterkonstanten nach Straumanis aus Äquatorinterferenzen hoher Beugungswinkel auf Schwenkaufnahmen — symmetrisch zu den drei rhombischen Achsen — ermittelt (Tabelle 1).

Tabelle 1. *Gitterkonstanten*

	Cer-tetrakis-(dibenzoyl-methan)	Thorium-tetrakis-(dibenzoyl-methan)	Uran-tetrakis-(dibenzoyl-methan)
a (Å)	10,320±0,002	10,398±0,002	10,303±0·002
b (Å)	20,109±0,003	20,298±0,003	20,136±0,003
c (Å)	23,514±0,005	23,334±0,005	23,613±0,005

Die Statistik der vorhandenen Interferenzen (hkl alle Ordnungen, $hk0$ mit $h+k = 2n$, $h0l$ mit $l = 2n$, $0kl$ mit $l = 2n$) führt zu der wahrscheinlichen Raumgruppe D_{2h}^{10}–$Pccn$.

Bei Annahme von 4 Molekülen in der Elementarzelle beträgt die Röntgendichte 1,52 g.cm.$^{-3}$ in Überein-