ordering are surrounded by atoms at a slightly greater distance than in the disordered state.

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The Structure of V_4Al_{23}*

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The crystal structure of the intermetallic compound V_4Al_{23} has been determined. The space-group symmetry was found to be D_{6h}^4–$P6_3/mmc$, and precision lattice parameters were measured as $a = 7{\cdot}692_8$ Å, $c = 17{\cdot}04_0$ Å. The compound is structurally related to Co_2Al_5, Fe_3NiAl_{10}, and Mn_3SiAl_9. The compound shows a pronounced, but imperfect, layering. Zone boundaries are prominent. Abnormally short Al–V bond distances were found.

Introduction

A phase diagram of the aluminum–vanadium system has been published by Carlson, Kenney & Wilhelm (1955). This diagram indicates the existence of four compounds in the system, and the printed discussion of the article leaves open the possible existence of a fifth compound. In view of the interest in the compounds of aluminum with transition metals (Pratt & Raynor, 1951; Raynor & Waldron, 1948; Raynor, 1949), an examination of the structures of these aluminum–vanadium compounds has been undertaken. A determination of the structure of the compound designated as the β-phase, tentatively identified in the foremention phase diagram as VAl_6, has been completed and is described in this paper.

Sample preparation

An arc-melted aluminum–vanadium alloy containing 6·7 wt.% vanadium was heated to 710° C. and held at temperature for 175 hr. in a beryllia vessel under a helium atmosphere. At the end of the heating period the sample was quenched in an oil bath. Optical examination of the alloy indicated the presence of two phases, aluminum plus a compound. The aluminum matrix was dissolved with 1NNaOH. The residue consisted of deep metallic blue crystals in the form of long hexagonal prisms. A representative sample of this residue was selected and analyzed for vanadium (Freeland & Fritz, 1955). The analysis showed 24·71± 0·18 wt.% vanadium. This result compares with a theoretical value of 23·94 wt.% vanadium for VAl_6 and of 24·72 wt.% vanadium for V_4Al_{23}. Spectrographic analysis of the crystals showed the presence of Cu, Mn, Fe, Si, and Ti as trace impurities.

* Contribution No. 491. Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission.

Cell dimensions and crystal symmetry

A back-reflection Weissenberg camera, similar to the one described by Buerger (1942), was used to obtain precision lattice constants. A hexagonal unit cell was found with dimensions

$$a = 7{\cdot}692_8 \text{ Å}, \quad c = 17{\cdot}04_0 \text{ Å}.$$

The measured density was found to be 3·089 g.cm.$^{-3}$ while the density calculated on the basis of 46 aluminum atoms and 8 vanadium atoms per unit cell is 3·134 g.cm.$^{-3}$.

Weissenberg patterns of the reciprocal space lattice taken about the unique axis showed C_{6l} symmetry for all observed levels, $l = 0$ through $l = 10$. Thus Laue symmetry D_{6h} was indicated. No systematic extinctions were observed in (hkl) or $(h0l)$ reflections, but (hhl) reflections occurred only with $l = 2n$. The Laue symmetry and extinction information limited the possible space groups to D_{6h}^4–$P6_3/mmc$, C_{6v}^4–$P6_3mc$, or D_{3h}^4–$P\bar{6}2c$. Three-dimensional intensity data were taken in order to select the proper space group. These data were obtained by a multiple-film technique, using Cu $K\alpha$ radiation and an equi-inclination Weissenberg camera. The intensities were estimated visually. The data were corrected for Lorentz and polarization factors in the manner of Lu (1943). A statistical examination of the intensity distribution was made, using the method of Howells, Phillips & Rogers (1950). The distribution curve is shown in Fig. 1 and indicates

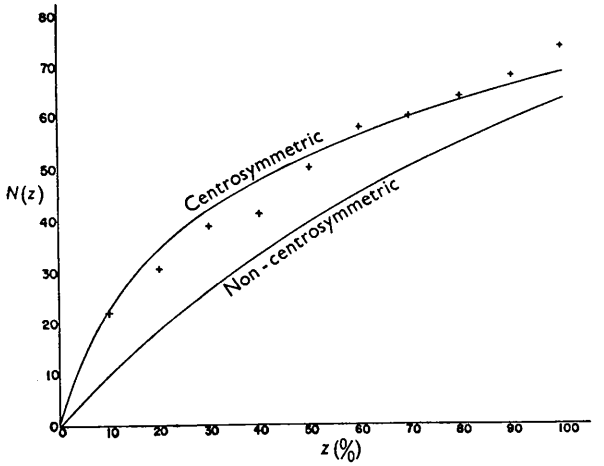

Fig. 1. Intensity distribution for the (*hkl*) reflections. The solid lines give the theoretical distributions. $N(Z)$ is the number of reflections with an intensity less than or equal to Z% of the local average intensity.

that the centrosymmetric space group, D_{6h}^4–$P6_3/mmc$, is the correct choice.

Structure determination

From the intensity data the following vector projections were made: $P(x, y)$, $P(x+y, z)$, $P(x, z)$, $P(x, y, 0)$, $P(x, y, \frac{1}{2})$, and $P(x, 0, z)$. The projections indicated imperfect layering in the [110] direction. Further interpretation indicated that most of the atoms were in positions with x, y coordinates of the type x, $2x$ with x approximately 7/60, 13/60, or 27/60. Values indicated for z coordinates were of the order of 1·5/60, 7/60, 10/60, and 15/60. These coordinates were utilized to construct a trial structure which satisfactorily matched the vector projections. This trial structure corresponded to the formula V_4Al_{23}. Spatial considerations ruled out the possibility of utilizing another two-fold position for aluminum atoms and hence eliminated the formula VAl_6.

Additional intensity data were taken in order to refine the trial structure. The single crystal used for the recording of these data was a hexagonal prism measuring 0·4 mm. in length and 0·05 mm. in diameter. The intensities of the (*h*0*l*) and (*hhl*) reflections were measured visually from timed exposures taken with a precession camera, using Mo $K\alpha$ radiation. A Geiger–Müller tube attachment to a Weissenberg camera was employed to measure the intensities of the (*hk*0) reflections with Cu $K\alpha$ radiation. The intensities were put on an absolute scale, using the method described by Wilson (1942). The three-dimensional intensity data taken with Cu radiation were not used for the final structure refinement because of the difficulty in making adequate absorption correction.

Fourier projections were made on the basis of the trial structure. Good agreement was obtained between the resulting projections and the postulated structure. The atomic parameters were refined by difference Fourier projections, using the graphical technique described by Lipson & Cochran (1953). Three successive refinements were necessary. The best values for the structure parameters are as follows:

2 V_1	in	2(*a*):	0, 0, 0	parameterless;
6 V_2	in	2(*h*):	x, $2x$, $\frac{1}{4}$	with $x = 0{\cdot}781 \pm 0{\cdot}002$;
12 Al_1	in	12(*k*):	x, $2x$, z	with $x = 0{\cdot}213 \pm 0{\cdot}003$ and $z = 0{\cdot}029 \pm 0{\cdot}001$;
12 Al_2	in	12(*k*):	x, $2x$, z	with $x = 0{\cdot}124 \pm 0{\cdot}003$ and $z = 0{\cdot}618 \pm 0{\cdot}001$;
12 Al_3	in	12(*k*):	x, $2x$, z	with $x = 0{\cdot}455 \pm 0{\cdot}003$ and $z = 0{\cdot}166 \pm 0{\cdot}001$;
6 Al_4	in	6(*h*):	x, $2x$, $\frac{1}{4}$	with $x = 0{\cdot}126 \pm 0{\cdot}002$;
4 Al_5	in	4(*f*):	$\frac{1}{3}$, $\frac{2}{3}$, z	with $z = 0{\cdot}167 \pm 0{\cdot}001$.

Evaluation of the standard deviations of the atomic parameters was based on the formulae of Cruickshank (1949). The final electron-density projection, $\varrho(x, z)$,

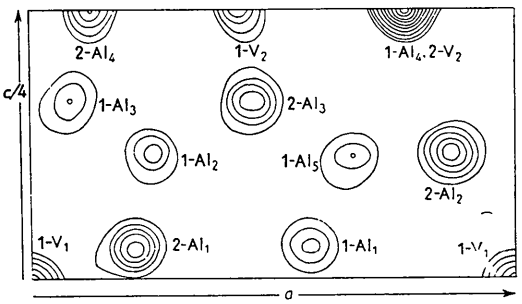

Fig. 2. The asymmetric unit of the final (*h*0*l*) electron-density projection without the use of an artificial convergence factor. The contours are drawn at intervals of 400 arbitrary units.

is shown in Fig. 2. No artificial convergence factor was used in making this projection.

Calculated structure factors based on the above parameters are compared with observed structure factors in Table 1. The reliability index

$$R = \Sigma||F_o|-|F_c||\div\Sigma|F_o|$$

based on the values in Table 1 is 0·14 for (*h*0*l*) data, 0·12 for (*hhl*) data, and 0·17 for (*hk*0) data. In computing these index values, the most intense low-angle

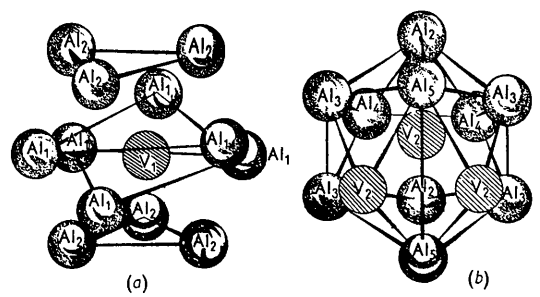

Fig. 3. The atomic arrangement (*a*) about the V_1 atoms, (*b*) about the V_2 atoms.

Table 1. *Observed and calculated structure factors for* V_4Al_{23}

hk.l	Fobs	Fcalc	hk.l	Fobs	Fcalc	hk.l	Fobs	Fcalc	hk.l	Fobs	Fcalc
002	--	-78	302	88	+78	5,0,18	92	-90	116	20	+20
004	101	+83	303	219	+226	5,0,19	88	-101	118	41	+41
006	< 12	-2	304	35	-35	5,0,20	23	+28	1,1,10	55	+52
008	212	+204	305	27	-20	600	78	-84	1,1,12	< 12	-2
0,0,10	135	-121	306	33	+27	601	75	+81	1,1,14	31	+27
0,0,12	97	+82	307	58	+49	602	38	+50	1,1,16	35	+33
0,0,14	223	-216	308	30	-31	603	148	-145	1,1,18	36	+35
0,0,16	105	+82	309	< 11	-3	604	24	-27	1,1,20	17	+14
0,0,18	< 12	-9	3,0,10	101	+108	605	23	+14	1,1,22	25	+31
0,0,20	< 12	-18	3,0,11	259	+274	606	34	+20	220	175	+162
0,0,22	177	-174	3,0,12	34	-34	607	35	-39	222	14	+12
0,0,24	162	+140	3,0,13	99	-106	608	< 12	-12	224	< 12	-6
100	32	+25	3,0,14	115	+117	609	17	+7	226	25	+29
101	50	+10	3,0,15	37	+44	6,0,10	72	+77	228	103	+89
102	50	+41	3,0,16	< 12	+14	6,0,11	161	-188	2,2,10	< 13	+12
103	50	-43	3,0,17	35	-24	6,0,12	< 12	-25	2,2,12	15	+9
104	20	+17	3,0,18	53	+54	6,0,13	72	+76	2,2,14	66	-62
105	< 12	+14	3,0,19	52	+60	6,0,14	71	+79	2,2,16	36	+42
106	24	-28	3,0,20	13	+19	6,0,15	34	-40	2,2,18	41	+33
107	163	-165	3,0,21	93	-85	6,0,16	< 12	+14	2,2,20	< 11	-5
108	87	+82	3,0,22	68	+81	6,0,17	32	+21	330	269	+363
109	< 12	+3	400	44	+39	6,0,18	38	+41	332	43	-35
1,0,10	61	+53	401	26	+42	700	11	+13	334	61	+50
1,0,11	< 12	-10	402	< 11	+22	701	24	-27	336	15	+1
1,0,12	< 11	-16	403	39	+43	702	< 11	+4	338	145	+169
1,0,13	18	-26	404	103	+110	703	< 11	+16	3,3,10	71	-79
1,0,14	17	+26	405	21	-35	704	< 11	-17	3,3,12	70	+62
1,0,15	83	-77	406	49	+33	705	< 11	0	3,3,14	159	-166
1,0,16	69	+67	407	22	+26	706	< 11	+12	3,3,16	71	+62
1,0,17	37	+16	408	< 11	+7	707	35	-18	3,3,18	< 11	+10
1,0,18	< 12	+15	409	< 11	+18	708	25	+25	3,3,20	18	-5
1,0,19	< 13	-9	4,0,10	24	-23	709	< 11	-14	440	50	+37
1,0,20	27	+24	4,0,11	24	+23	7,0,10	36	+30	442	23	+14
1,0,21	52	+43	4,0,12	71	+63	7,0,11	31	+31	444	< 9	-2
1,0,22	16	+16	4,0,13	< 12	+12	7,0,12	< 12	+12	446	< 10	+8
200	54	-47	4,0,14	< 12	+3	7,0,13	< 11	-28	448	< 10	+8
201	42	+37	4,0,15	< 12	-6	7,0,14	18	+26	4,4,10	52	+47
202	14	+8	4,0,16	< 12	-6	7,0,15	< 11	+1	4,4,12	10	-5
203	15	-13	4,0,17	19	-24	7,0,16	37	+33	4,4,14	55	+47
204	52	+43	4,0,18	18	-30	800	24	+29	4,4,16	25	+22
205	68	-63	4,0,19	25	+33	801	< 11	+2	550	158	+160
206	176	+151	4,0,20	30	+31	802	< 11	+1	552	< 10	+1
207	123	-91	500	42	+35	803	34	+15	554	< 10	-2
208	130	+101	501	85	+76	804	17	-21	556	18	+15
209	30	-30	502	72	+71	805	31	+31	558	66	+78
2,0,10	36	+26	503	112	-109	806	34	-39	120	58	+37
2,0,11	37	-26	504	161	+169	807	107	+122	130	22	-16
2,0,12	106	+93	505	144	+132	808	65	+72	140	61	+59
2,0,13	39	-28	506	< 11	+6	809	< 11	+4	150	34	-31
2,0,14	101	+93	507	< 12	+13	8,0,10	44	+42	160	37	+41
2,0,15	60	-49	508	27	+26	8,0,11	14	+10	170	133	+127
2,0,16	38	-39	509	< 11	+1	8,0,12	13	-19	230	31	+31
2,0,17	< 13	+5	5,0,10	28	-23	900	125	+176	240	12	+5
2,0,18	53	+94	5,0,11	50	-56	901	< 11	-3	250	69	-31
2,0,19	27	+26	5,0,12	18	+21	902	19	-19	260	41	+38
2,0,20	< 13	+7	5,0,13	< 12	+1	903	< 11	+8	270	51	-17
2,0,21	35	+27	5,0,14	< 12	+13	904	42	+40	340	8	-8
2,0,22	63	+55	5,0,15	37	+29	110	20	+25	350	29	-30
300	179	-154	5,0,16	< 12	-18	112	50	+48	360	55	-52
301	121	-124	5,0,17	59	+60	114	< 12	-1	450	72	+68

reflection, (330), is omitted. Temperature factors of 0·34 Å^2 for the (*h*0*l*) data and 0·50 Å^2 for the (*hhl*) data were found to give the best agreement between observed and calculated structure factors. The (*hk*0) data were not corrected for the temperature factor.

Fig. 3 shows the atomic arrangements about the two types of vanadium positions, V_1 and V_2, respectively. In Fig. 3(*a*) the V_1 atom is situated at the origin. The connected aluminum atoms lie in planes normal to the *c* axis and are related by a 6_3 screw axis. In Fig. 3(*b*) the V_2 atoms are related by a threefold rotation axis in the [001] direction passing through the Al_5 atoms. The V_2 and Al_4 atoms lie on a plane normal to and one-quarter along the *c* axis. An interesting feature of the clustering around the two types of vanadium atoms is that in both cases the surrounding atoms approximate regular icosahedra. Pauling (1947) has pointed out that the most efficient C.N. 12 packing is represented by a regular icosahedron if the radius of the central sphere is 0·901 times the radius of spheres at the vertices of the icosahedron. The radius ratio of vanadium to aluminum is 0·923.

Each atom in the structure has twelve neighbors within 3·0 Å. Table 2 lists the interatomic distances. The average values for the Al–Al and V–V bonds in the structure are the same as in the pure metals, 2·86 Å and 2·64 Å, respectively. The mean Al–V bond distance is 2·72 Å, while that predicted on the basis of the interatomic distances in the pure metals

Table 2. *Interatomic distances in* V_4Al_{23}

Atom	Neighbor	No. of neighbors	Distance (Å)	Probable error (Å)
V_1	Al_1	6	2·88	0·020
	Al_2	6	2·60	0·025
V_2	V_2	2	2·64	0·020
	Al_2	2	2·58	0·035
	Al_3	4	2·83	0·035
	Al_4	2	2·54	0·025
	Al_5	2	2·73	0·030
Al_1	V_1	1	2·88	0·020
	Al_1	2	2·78	0·025
	Al_1	2	3·00	0·030
	Al_2	2	2·77	0·035
	Al_2	2	2·90	0·035
	Al_3	2	2·84	0·040
	Al_5	1	2·96	0·030
Al_2	V_1	1	2·60	0·025
	V_2	1	2·58	0·035
	Al_1	1	2·77	0·030
	Al_1	2	2·90	0·030
	Al_2	2	2·86	0·030
	Al_3	2	2·92	0·035
	Al_4	2	2·80	0·030
	Al_5	1	2·79	0·025
Al_3	V_2	2	2·83	0·035
	Al_1	2	2·84	0·040
	Al_2	2	2·92	0·035
	Al_3	2	2·81	0·035
	Al_3	1	2·86	0·030
	Al_4	2	2·80	0·030
	Al_5	1	2·95	0·025
Al_4	V_2	2	2·54	0·025
	Al_2	4	2·80	0·030
	Al_3	4	2·80	0·030
	Al_4	2	2·91	0·020
Al_5	V_2	3	2·73	0·030
	Al_1	3	2·96	0·030
	Al_2	3	2·79	0·025
	Al_3	3	2·95	0·025

is 2·77 Å. The 2·77 Å distance is computed for C.N. 12 using the formula of Pauling (1947). The volume occupied by the Al and V atoms in V_4Al_{23} is 0·3% less than the volume these atoms would occupy in the pure metals. The shortest observed bond distance is 2·54 Å for the Al_4–V_2 bond. The only other compound in the aluminum–vanadium system whose structure has been determined is VAl_3 (Brauer, 1943). In VAl_3 the average Al–V bond is 2·74 Å and the shortest Al–V bond is 2·67 Å. Thus the aluminum-rich V_4Al_{23} has some significantly shorter Al–V bonds than those occurring in VAl_3.

Discussion

The structure of V_4Al_{23} is closely related to the structures of Co_2Al_5 (Bradley & Cheng, 1938), Fe_3NiAl_{10} (Bradley & Taylor, 1940), and Mn_3SiAl_9 (Robinson, 1952). Robinson has examined the geometry of the Brillouin zone for these structures and has found that

an inscribed prolate spheroid in the zone should fill at an electron/atom ratio near 1·68. It has been pointed out by Robinson and also by Taylor (1954) that the most stable composition for some of the aluminum–transition-element compounds is non-stoichiometric and occurs with a deficit of transition element atoms. Apparently no such deficit occurs in V_4Al_{23}. In the phase diagram V_4Al_{23} is shown as a line compound with negligible composition variation, and the forementioned chemical analysis indicates that this composition is stoichiometric. Table 3 shows the computed electron/atom ratios for V_4Al_{23} and the related compounds at stoichiometry and at the estimated stable composition.

Table 3. *Electron/atom ratios for* V_4Al_{23} *and related compounds**

Compound	Electron/atom ratio (Stoichiometric)	Electron/atom ratio (Non-stoichiometric)
V_4Al_{23}	1·72	—
Mn_3SiAl_9	1·54	1·78 (19·60 at.% Mn, 8·88 at.% Si; Robinson) 1·59 (22.05 at.% Mn, 6·50 at.% Si; Taylor)
Co_2Al_5	1·65	1·72 (27·2 at.%; Robinson, Taylor)
Fe_3NiAl_{10}	1·53	1·68 (17·7 at.% Fe, 8·7 at.% Ni; Robinson)

* Computed with the following values for valence:

Al +3	V −5·66	Fe −2·66	Ni −0·61
Si +4	Mn −3·66	Co −1·71	

The consistency of the electron/atom ratios at stable composition lends support to arguments based on zone theory. Of the four structures in question only Co_2Al_5 and Fe_3NiAl_{10} are isomorphous. However, all four of the structures have the same space group symmetry which gives rise to identical Brillouin zone geometry.

The transition metal configuration in the above four structures has one feature in common: three transition metal atoms are bonded as nearest neighbors in an equilateral triangle. This differs from most of the aluminum–transition-metal structures in that the transition metal atoms are not usually nearest neighbors. Other common characteristics of aluminum–transition-element structures are exhibited by these four compounds. These include layering, short aluminum–transition-metal bond distances, and prominent zone boundaries. In V_4Al_{23} the layering occurs normal to the [110] and [120] directions.

Black (1956) has discussed the structural relationships between the compounds of aluminum with transition elements. He has noted a trend of an increase in coordination to aluminum with decreasing atomic number of the transition element: from eight aluminum atoms coordinated to copper to ten aluminums coordinated to manganese. The coordination in V_4Al_{23} is consistent with this trend; 25% of the vanadium atoms are coordinated to twelve aluminums and 75% of the vanadium atoms are coordinated to ten aluminums.

Measurements of magnetic susceptibility by Föex & Wucher (1954) indicate that in aluminum–transition-element compounds pairing of the *d* electrons occurs. On this basis V_4Al_{23} would be expected to be weakly paramagnetic with little temperature dependence. The filling of non-bonding sub-shells and the contraction of bond distances seem somewhat contradictory, and hence the evidence supports the view that the *d* electrons are involved in the bonding. This is not inconsistent with the susceptibility measurements of Föex & Wucher since, as a first approximation (Wilson, 1953), temperature-independent paramagnetism is a function only of the Fermi level. The introduction of transition metal atoms into aluminum with the high density of states in the *d* levels would tend to lower the Fermi level. Hence, a susceptibility less than pure aluminum observed in $CrAl_7$ and $MnAl_6$ is not unreasonable and might also be expected in V_4Al_{23}.

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