Type $6H$ is known to occur very commonly and is regarded as the most stable modification of silicon carbide. Thus it is significant to note that in both cadmium iodide and silicon carbide, the basic types ($4H$ and $6H$ respectively) possess a higher symmetry than expected. At present it is very difficult to say what provides the ordering forces which bring about this intriguing situation. However, the restriction of the hexagonal symmetry to only small cells (the largest being $8H$ with $c = 20\cdot14$ Å) in silicon carbide appeared to suggest that these ordering forces, whatever their nature may be, could operate over only small distances. But the present discovery of hexagonal symmetry in a cell as large as $24H$ ($c = 82\cdot02$ Å) in cadmium iodide shows that the forces can indeed be operative over fairly large distances.

Crystal no. 1, found to be a combination of types $8H_b$ and $4H$ in syntactic coalescence with each other, shows that the structure transformed from $8H$ to $4H$ during growth (the lower face of the crystal, as picked up from the crystallizing dish, was found to be $8H$). The same is the case with crystal no. 2, which is found to be a combination of types $24H_g$ and $24H_h$, with the difference that the cell dimensions have remained unchanged during the transformation. However, recent work (Chadha & Trigunayat, 1967a) has shown that such transformations are observed very frequently in cadmium iodide. The two somewhat similar cases,

($30R + 30H$) and ($42R + 42H$), have been discussed earlier in detail by Chadha & Trigunayat (1967b), who concluded that the transformations can be understood on the basis of the layer transposition mechanism of Jagodzinski (1954). The present two cases of structure transformation can be explained on the same lines.

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The Structures of Two Polymorphic Forms of YAl₃*

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Two structurally related polymorphic forms of YAl₃ have been corroborated: a low temperature form with the hexagonal Ni₃Sn-type structure and a high temperature form with a rhombohedral BaPb₃-type structure. The principal factor influencing the stability of the polymorphs appears to be the conservation of relatively short Al–Al bonds. The layered high temperature polymorph is subject to frequent faulting of the form previously observed in samarium.

Introduction

In an investigation of the aluminum-rich end of the yttrium–aluminum system, Savitsky (1959) reported that Y₂Al₅ is the phase most rich in aluminum. The entire system was investigated by Snyder (1960) who noted YAl₃ as the most aluminum-rich phase. Snyder's equilibrium diagram for the system is shown in Fig. 1. Lundin & Klodt (1961) substantially corroborate Snyder's work and, on the basis of X-ray powder data,

tentatively indicate YAl₃ to be hexagonal. Snyder, however, observed two distinct growth habits in crystals selected from a furnace-cooled alloy, *i.e.* needle-shaped crystals of approximately square cross section and truncated hexagonal bipyramids in degrees of development varying from hexagonal platelets to approximately equiaxed shapes. By examining crystals from furnace-cooled alloys of several compositions Snyder found that as the aluminum content of the alloy increased (corresponding, according to Fig. 1, to a reduced initial temperature of precipitation of the phase) the percentage of needle-shaped crystals present increased. He was unable to prepare alloys containing only needle-shaped crystals in any alloy richer in yttrium

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than the eutectic composition. He thus concluded that the needle form of the phase is the low temperature form and that the transformation temperature is quite close to the eutectic temperature, 640°C. On the basis of preliminary powder and single-crystal diffraction work by the present author, Snyder reported the low temperature needle form of YAl₃ to be an isotype of Ni₃Sn, DO_{19} (see Pearson, 1958) with $a=6\cdot31$, $c=4\cdot58$Å and the high temperature form to hexagonal with $a=6\cdot31$, $c=21\cdot34$ Å.

Subsequently Bruzzone & Ruggiero (1962) reported from powder data a rhombohedral cell for YAl₃ with lattice parameters (hexagonal basis) $a=6\cdot195$, $c=21\cdot17$ Å. No evidence of the low temperature polymorph was found by van Vucht & Buschow (1965) who attributed the earlier observation of this form to differences in sample preparation techniques. On the basis of powder data these authors found the structure of YAl₃ to be the rhombohedral BaPb₃ structure reported by Sands, Wood & Ramsey (1964) with lattice parameters (hexagonal basis) $a=6\cdot194$, $c=21\cdot138$ Å. Recently, Dagerhamn & Westman (1966) have refined the positional parameters of this structure from Weissenberg single-crystal X-ray data and have measured the lattice parameters $a=6\cdot19_5$, $c=21\cdot12_9$ Å from powder data obtained with a Guinier camera.

The work presented herein details the structure investigation of the low temperature polymorph of YAl₃ and confirms the refinement of the positional parameters of the high temperature polymorph, thus conclusively establishing the existence of the two polymorphs of YAl₃.

Low temperature polymorph

A furnace-cooled 30 wt% yttrium alloy prepared in an alumina crucible was treated with hot sodium hydroxide yielding a residue of crystals. A needle-shaped crystal of dimensions approximately $60 \times 60 \times$
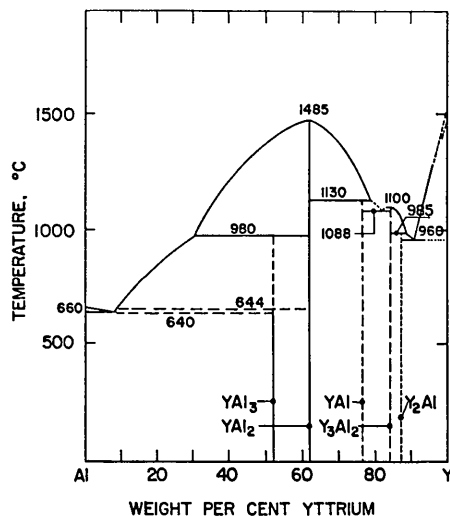

Fig. 1. The yttrium-aluminum phase diagram (Snyder, 1960).

110 microns was selected from this residue and mounted for X-ray examination. The D_{6h} diffraction symmetry and characteristic extinction conditions (hhl and $00l$ observed only when $l=2n$) indicated probable space groups $P6_3/mmc$, $P\bar{6}2c$ and $P6_3mc$. Extrapolation against the Nelson & Riley (1945) function of Cu $K\alpha$ ($\lambda\alpha_1=1\cdot54051$ Å) powder data obtained from crushed needle-shaped crystals from the same alloy residue yielded lattice parameters $a=6\cdot276\pm0\cdot002$, $c=4\cdot582\pm0\cdot001$ Å.

Relative intensity data for 30 $h0l$ reflections were obtained by the 2θ scan technique with a General Electric single-crystal orienter equipped with a scintillation counter. Cu $K\alpha$ radiation was employed. Standard corrections for Lorentz and polarization effects were applied but no correction was made for absorption effects. On the basis of the similarity of the lattice parameters of their tri-aluminides the ThAl₃ (Ni₃Sn; see Pearson, 1958) structure was chosen as a trial structure for YAl₃. This trial structure was refined on an IBM 7074 computer with the least-squares program of Busing, Martin & Levy (1962). The atomic form factors of Thomas & Umeda (1957) were employed without correction for the effects of anomalous dispersion. The refinement to the structure given below produced a residual $R=\Sigma\ ||F_o|-|F_c||/\Sigma\ |F_o|=0\cdot099$ with all 30 reflections given unit weight.

Space group $P6_3/mmc$

with 2Y at $\pm(\frac{2}{3},\frac{1}{3},\frac{1}{4})$

and 6Al at $\pm(x,2x,\frac{1}{4}; 2\bar{x},\bar{x},\frac{1}{4}; x,\bar{x},\frac{1}{4})$

with $x=0\cdot1466\pm0\cdot0002$.

Isotropic temperature factors $B_Y=0\cdot16\pm0\cdot12$ Å² and $B_{Al}=1\cdot38\pm0\cdot39$ Å² were obtained. A comparison of observed and calculated structure factors is given in Table 1.

Table 1. *Comparison of observed and calculated structure factors for low temperature* YAl₃

$h0l$	F_o	F_c	$h0l$	F_o	F_c
100	2·09	−2·12	402	6·40	5·66
200	8·07	−8·19	502	5·09	4·85
300	5·43	5·30	602	7·34	−7·21
400	5·15	−6·23	103	6·56	−4·97
500	4·46	−5·26	203	12·45	11·30
600	7·23	7·71	303	3·12	2·78
101	7·01	6·78	403	8·34	−8·40
201	12·18	−14·60	503	1·65	1·36
301	3·66	−3·47	004	13·33	12·19
501	1·41	−1·32	204	6·76	−5·53
601	—	0·55	304	4·64	3·85
002	16·45	−17·28	404	5·07	−4·48
102	2·49	1·82	105	3·84	3·75
202	8·51	7·48	205	7·98	−8·13
302	5·58	−4·71	305	1·98	−1·92

High temperature polymorph

A crystal of platelet growth habit was selected from the same alloy residue which yielded the crystal of the low temperature polymorph and was mounted so that

it rotated around the normal to the plate surface when examined with a Weissenberg camera. Ten layers of qualitative Cu $K\alpha$ data were taken. These data contained the apparent diffraction symmetry and characteristic extinctions of space groups $P6_3/mmc$, $P\bar{6}2c$ and $P6_3mc$ with the exception that when $l=3n$, only $-h+k+l=3n$ reflections were observed. Examination of other crystals of similar growth habit and of hexagonal bipyramid form showed that the rotational symmetry was in fact threefold, but for $l\neq3n$ reflections of the type $-h+k+l\neq3n$ occurred with weaker intensity than those of the $-h+k+l=3n$ type. The relative intensities of the 'rhombohedrally forbidden' reflections compared with those of the 'allowed' reflections varied from crystal to crystal. These observations led to the conclusion that the true diffraction symmetry and characteristic extinction conditions of the high temperature polymorph were those of space groups $R\bar{3}m$, $R3m$ and $R32$ although these were generally partially masked by the effects of faulting. After some perseverance in selecting crystals, a nearly equiaxed bipyramid was found which appeared unfaulted. This crystal, with a diameter of approximately 130 microns, was subsequently used to gather relative intensity data for 73 $h0l$ reflections in the same manner as was employed for the low temperature polymorph. The Cu $K\alpha$ data were corrected for Lorentz and polarization effects and for absorption effects based upon a spherical approximation. The $BaPb_3$ structure suggested by van Vucht & Buschow and subsequently refined by Dagerhamn & Westman was chosen as a trial structure. The atomic form factors of Cromer & Weber (1965) were corrected for anomalous dispersion (*International Tables for X-ray Crystallography*, Vol. 3, p. 214) and were used in the refinement of this trial structure with the program of Busing *et al.* The refined structure given below is in good agreement with that of Dagerhamn & Westman and yielded a residual $R=0.087$ with all 73 reflections weighted equally. Additional positional parameters introduced by representing the trial structure in the lower symmetry space groups in all cases refined to, within experimental uncertainty, the invariant parameters of space group $R\bar{3}m$.

Space group $R\bar{3}m$

with 3Y at $(0,0,0; \frac{2}{3},\frac{1}{3},\frac{1}{3}; \frac{1}{3},\frac{2}{3},\frac{2}{3})$

6Y at $(0,0,0; \frac{2}{3},\frac{1}{3},\frac{1}{3}; \frac{1}{3},\frac{2}{3},\frac{2}{3})$

$\pm(0,0,z)$ $z=0.2190\pm0.002$

9 Al at $(0,0,0; \frac{2}{3},\frac{1}{3},\frac{1}{3}; \frac{1}{3},\frac{2}{3},\frac{2}{3})$

$+(\frac{1}{2},0,0; 0,\frac{1}{2},0; \frac{1}{2},\frac{1}{2},0)$

and 18 Al at $(0,0,0; \frac{2}{3},\frac{1}{3},\frac{1}{3}; \frac{1}{3},\frac{2}{3},\frac{2}{3})$

$\pm(x,2x,z; 2\bar{x},\bar{x},z; x,\bar{x},z)$

with $x=0.4770\pm0.0009$

and $z=0.2223\pm0.0004$.

Isotropic temperature factors $B_Y=0.41\pm0.23$ Å^2 and 0.17 ± 0.14 Å^2 for the yttrium threefold and sixfold atom sets, respectively, and $B_{Al}=0.60\pm0.72$ Å^2 and

2.11 ± 1.02 Å^2 for the aluminum ninefold and eighteenfold atom sets, respectively, were computed. Observed and calculated structure factors are compared in Table 2. Lattice parameters (hexagonal basis) $a=6.204\pm0.002$, $c=21.184\pm0.007$ Å were obtained by Nelson & Riley (1945) extrapolation of Cu $K\alpha$ ($\lambda\alpha_1=1.54051$ Å) powder data.

Table 2. *Comparison of observed and calculated structure factors for high temperature* YAl$_3$

h0ℓ	F_o	F_c	h0ℓ	F_o	F_c	h0ℓ	F_o	F_c
300	36.89	36.21	3̄06	18.69	18.15	0,0,12	7.90	-6.71
600	40.53	41.53	606	8.77	8.07	3,0,12	6.40	6.25
101	16.49	15.09	6̄06	4.81	4.04	3̄,0,12	17.79	-15.80
2̄01	51.74	55.96	107	12.28	-12.07	6,0,12	1.64	-1.50
401	35.03	37.62	2̄07	33.77	-30.75	6̄,0,12	1.72	1.86
5̄01	26.62	26.54	407	14.01	-17.04	1,0,13	28.60	26.70
1̄02	11.51	-10.95	5̄07	13.60	-10.87	2̄,0,13	68.36	64.99
202	32.35	-32.47	1̄08	7.71	5.71	4,0,13	48.22	43.24
4̄02	19.67	-16.81	208	42.48	40.94	5̄,0,13	7.37	6.87
502	10.32	-10.18	4̄08	33.71	29.03	1̄,0,14	37.07	36.43
003	3.28	-2.65	508	21.31	20.07	2,0,14	71.37	71.59
303	14.86	13.60	009	107.48	117.93	4̄,0,14	54.01	48.95
3̄03	14.86	-13.60	309	30.53	30.93	5,0,14	17.05	13.32
603	2.00	1.15	3̄09	30.95	31.08	6,0,15	7.62	8.43
6̄03	4.68	5.40	609	36.40	37.01	3,0,15	1.42	-1.71
104	43.91	44.69	6̄09	36.17	36.98	3̄,0,15		16.95
2̄04	92.37	96.17	1,0,10	18.05	18.95	1,0,16	7.51	-8.97
404	57.70	59.35	2̄,0,10	55.83	49.77	2̄,0,16	25.87	-21.33
5̄04	10.39	9.76	4,0,10	38.03	36.19	4,0,16	11.16	-13.11
1̄05	51.22	48.86	5̄,0,10	31.82	26.65	5̄,0,16	10.85	-8.99
205	91.10	98.43	1̄,0,11	6.66	-5.39	1̄,0,17	0.13	-0.43
4̄05	64.31	61.61	2,0,11	22.59	-21.99	2,0,17	24.55	22.36
505	14.73	12.38	4̄,0,11	13.57	-11.96	4̄,0,17	16.62	16.78
006	6.05	4.99	5,0,11	7.79	-7.01	5,0,17	11.71	11.51
306	9.67	-9.20						

Discussion

In their examination of the trialuminides of the lanthanide series of rare earths, van Vucht & Buschow found the cubic Cu_3Au structure for the trialuminides of the smaller members of the series, Er, Tm and Yb, and the hexagonal Ni_3Sn structure for the trialuminides of the larger members, La, Ce, Pr, Nd, Sm and Gd. Intermediate stacking combinations of these structure types exist for the trialuminides of Y, Tb, Dy and Ho. The relationship between these structures may be seen by first considering the cubic $ErAl_3$ (Cu_3Au-type) structure which requires that all nearest-neighbor distances be equal in length, *i.e.* the Al–Al bond lengths are identical with the Er–Al bond lengths, 2.98 Å (Table 3). The substitution of a larger atom for Er requires the lengthening of all bonds and the resulting increase in the Al–Al bond lengths reduces the strength of these bonds resulting in structure instability. Thus, by implication from the work of van Vucht & Buschow, the largest average Al–Al bond length which permits a stable structure of the Cu_3Au type in the series of trialuminides is that of $ErAl_3$, 2.98 Å.

The rhombohedral structure of high temperature YAl_3 may be visualized as a stacking modification of the $ErAl_3$ structure where the right-handed screw rotation of layers in $ErAl_3$, ABC/ABC, becomes a right-handed 'ratchet' with nine-layer periodicity in YAl_3, $ABABCBCAC/AB$. The layers at 0/9, 3/9 and 6/9 in the latter structure retain their uniformly spaced cubic arrangement of atoms. In the remaining layers the aluminum atoms shift within the layer sacrificing some Al–Al bonds to shorten the remaining bonds giving a hexagonal nature to these layers. The yttrium atoms of the hexagonal layers shift slightly toward the voids

in the adjacent hexagonal layer which were introduced by the shift in aluminum positions and thus preserve close Y–Al bonding. Bond distances tabulated in Table 3 show that the resulting average bond distances equal the assumed maximum 2·98 Å with many of the bonds being substantially shorter.

A left-handed 'ratchet' model for high temperature YAl₃ may be chosen by rotating the origin of the cell 180° around the threefold axis. A mixture of the left-handed and right-handed stacking arrangements in a single crystal would introduce little distortion and would adequately explain the faulting and observation of 'forbidden' reflections from most of the crystals examined in the present investigation. This model for the faulting mechanism is identical with that found for the similar samarium structure by Daane, Rundle, Smith & Spedding (1954) except that in the present case the two stacking modifications are present in varying amounts.

In the low temperature YAl₃ structure the aluminum atoms in the hexagonal layers adjust by a greater amount, allowing the yttrium atoms to remain coplanar in the layer thus forming the two-layer hexagonal Ni₃Sn-type structure. This arrangement also results in reducing the length of a number of Al–Al bonds and preserves the average length 2·98 Å for these bonds (Table 3).

The failure of other investigators to observe the low temperature polymorph of YAl₃ may be explained by Snyder's observation that residues of alloys of composition near that of YAl₃ consisted primarily of the high temperature polymorph. Evidence of small amounts of the low temperature polymorph could be easily masked in the profusion of lines from the high temperature form by line overlap in powder investigations. Dagerhamn & Westman prepared their material by arc-melting, which probably resulted in a cooling rate too fast to permit the formation of the low temperature form.

The nature of the transformation in YAl₃ is not established. Attempts to transform the high temperature form to the low temperature form by annealing at 600 °C have failed. The close similarity of packing in the two polymorphs and resultant probable small difference in free energy may well preclude such transformation in reasonable annealing times. The possibility of the formation of the low temperature polymorph being a kinetic phenomenon has not been eliminated. Indeed, from Fig. 1, any formation of YAl₃ at temperatures near the eutectic temperature, 640 °C, must be from an aluminum-rich liquid which might well influence the growth kinetics.

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Table 3. *Interatomic distances for* ErAl₃ *and* YAl₃

ErAl₃ $a_0 = 4\cdot215$ Å*		Number of		High Temperature YAl₃†		Number of	
	Neighbor	neighbors	Distance		Neighbor	neighbors	Distance
Er	Al	12	2·98 Å	Y_c	Al$_c$	6	3·10 Å
					Al$_h$	6	3·11
Al	Er	4	2·98				
				Y_h	Al$_c$	3	3·01
	Al	8	2·98		Al$_h$	3	3·06
					Al$_h$	6	3·11
Low temperature YAl₃				Al$_c$	Y_c	2	3·10
					Y_h	2	3·01
Y	Al	6	3·15		Al$_c$	4	3·10 2·98 average
					Al$_h$	4	2·89
	Al	6	3·06				
				Al$_h$	Y_c	1	3·11
Al	Y	2	3·15		Y_h	1	3·06
					Y_h	2	3·11
	Y	2	3·06		Al$_c$	2	2·89
					Al$_h$	2	2·67
	Al	4	2·79		Al$_h$	2	2·82 2·97 average
					Al$_h$	2	3·53
	Al	2	2·76				
			2·96 average				
	Al	2	3·51				

* Buschow & van Vucht (1965).
† The subscripts *c* and *h* refer to atoms in layering of cubic and hexagonal character respectively.

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Anomalous Orientations of Cubic Close Packing in the Dehydration of Goethite in an Inert Atmosphere*

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Single-crystal X-ray studies of the dehydration of goethite (α-FeOOH) in an inert atmosphere (N_2) at relatively low temperatures (350–500 °C) showed that haematite (α-Fe$_2$O$_3$) and magnetite (Fe$_3$O$_4$) are both formed topotactically. The haematite has the same orientation as when it is formed on dehydration in air, but no satellite reflexions were observed. The magnetite is formed in eight different orientations. Two of these correspond to the normal orientations; for both [111] is parallel to [100] of goethite ([0001]$_{\text{h.c.p.}}$); one has (1$\overline{1}$0) parallel to (001) of goethite [(2$\overline{1}$$\overline{1}$0)$_{\text{h.c.p.}}$], and the other is rotated through 60° from this position. The other six orientations, all with [11$\overline{2}$] parallel to [100] of goethite ([0001]$_{\text{h.c.p.}}$) are interrelated by 60° rotations; one corresponds to (111) parallel to (010) of goethite [(1$\overline{1}$00)$_{\text{h.c.p.}}$], and the others are at 60, 120, 180, 240 and 300° from this orientation. General considerations are discussed regarding the mechanisms of transformations in structures based on hexagonal close packing and cubic close packing assemblages of atoms or ions. Normal orientations (first kind) and anomalous orientations (second kind) of close packing are derived from a slipping mechanism of the close-packed layers. Emphasis is put on the distinction between twinning derived from different orientations of the packing of the large ions, and twinning derived from different distributions of the interstitial ions inside the packing.

Introduction

Results for the dehydration of goethite (α-FeOOH) in air have been published by several authors (*e.g.* Goldsztaub, 1935; Francombe & Rooksby, 1959; Lima-de-Faria & Gay, 1962; Lima-de-Faria, 1963). The iron ion being so readily reduced, it was thought that dehydration in an inert atmosphere could give rise to results quite different from the previous ones. Their study is the subject of the following work.

X-ray single crystal work

The main results established for the dehydration of goethite (α-FeOOH) in air were the following: haematite (α-Fe$_2$O$_3$) is derived topotactically from goethite, with twinning developing during the transformation; inter-

mediate stages of the transformation are observed before the dehydration is completed. The intermediate stages are characterized by the occurrence of satellite spots and diffuse intensity regions around the strong haematite reflexions. An earlier stage of the dehydration in air with haematite satellites and a few reflexions of goethite still present is obtained on heat-treatment at 350 °C for 5 minutes (Lima-de-Faria, 1963). Therefore, the same temperature and time were used for a single crystal of goethite (0·8 mm long), but with a nitrogen atmosphere. A similar stage of dehydration was obtained in that haematite reflexions and some reflexions of residual goethite were observed, but no satellites were detected; on the other hand, extra reflexions were observed which could be ascribed to magnetite (Fe$_3$O$_4$). Further heating at 400 °C for 1 hour, or at 500 °C for 15 minutes, made the goethite reflexions disappear, while haematite and magnetite reflexions were observed. The haematite was in the same twinned orientation as when formed on dehydration of goethite in air.

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