matrix least-squares refinements of an overall scale factor and of positions and B's for all atoms except hydrogen, using unit weight for all reflections. The quantity minimized was $\Sigma\, w(F_o - F_c)^2$. In each case the refinement was continued until the maximum shift of any parameter was less than one-half of the estimated standard deviation.

The crystals were assumed to be bounded by {100}, {010} and {001}. The perpendicular distance between each set of parallel and opposite faces (l_1, l_2, l_3) was varied in different cases so as to give rise to four shapes of crystal, needles of small cross-section (shape I), needles of medium cross-section (shape II), plates (shape II), and nearly regular parallelepipeds (shape IV).

The results of the calculations on the smallest (labelled α) and largest (labelled ω) crystal of each of the shapes are listed in Table 1. Examination of the table shows the following general effects:

(1) For a given crystal shape, the isotropic temperature factors of all atoms are changed by essentially the same amount. In five of the seven cases listed, the change in B is many times larger than the estimated standard deviations.

(2) In the case of regular parallelepipeds (shape IV), as one goes from smaller to larger crystals the ΔB's, which are negative, increase in magnitude so much that, in crystal IVω, $B_{\rm Pd}$ has become negative. Such a trend would be expected, since a particular set of F_o's should show the average slope of the absorption correction line, and this would be related to the volume of the crystal. However, in the case of needles and plates, as one increases the length of the needle or the face area of the plate, ΔB becomes less negative. This is so because, in needles mounted about the needle axis, any increase in length affects a large number of high-angle reflections whereas most of the lower angle reflections are affected very little. This means a greater decrease in the intensity of a large number of high-angle reflections as compared with lower angle ones, which will show up in an increase of the B's. The same kind of behaviour will be observed if the face area of a plate mounted about one of its edges is increased.

(3) Some of the positional parameter changes are quite large (the largest being 0·16 Å for z of C(1) in case IIIω), but the estimated standard deviations are also large. Only seven of the 105 changes are $>\sigma$, only two are $>2\sigma$, and none are $>3\sigma$.

In another series of calculations we investigated the effect of introducing random errors into the set of F_o's. Eight cases were studied. In every case, introduction of a set of normally distributed random errors (mean$=0$, $\sigma=5\%$) caused R to increase somewhat, σ to increase slightly or not at all, and the shifts to become quite different although of about the same average magnitude. In two cases anisotropic refinement was carried out and, as might be expected, R decreased. The shifts in positional parameters changed, but in general there was no significant change in their average magnitude. Thus it appears that a part of the absorption error was compensated by changes in the B_{ij}'s. Presumably one could correlate the changes in shape and size of the vibration ellipsoids of different atoms with the changes in shape and size of the crystals but we have made no such study.

After this study was completed, a similar conclusion has been reported by Werner (1964).

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References

WERNER, P. (1964). *Acta Chem. Scand.* **18**, 1851.

WIESNER, J. R. & LINGAFELTER, E. C. (1966). To be published.

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Note on the nine-layer hexagonal structure of YAl$_3$.

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In the yttrium–aluminum system there occurs a phase of the composition YAl$_3$, reported to be rhombohedral, with hexagonal lattice parameters $a=6{\cdot}195$, $c=21{\cdot}17$ Å (Bruzzone & Ferro Ruggiero, 1962) or $a=6{\cdot}194$, $c=21{\cdot}138$ Å (van Vucht & Buschow, 1964). The latter authors assume the structure to be a nine-layer sequence to fit the c/a ratio.

The present investigation yields $a=6{\cdot}19_5$, $c=21{\cdot}12_9$ Å, $c/a=3{\cdot}41_1$, from X-ray Guinier powder photograph data for an alloy prepared from components weighed out to correspond to the composition YAl$_{3\cdot00}$. The weight loss in the arc-melting process of preparation was less than 1 % of the Al content. The phase appears to be stoichiometric. The structural principle has been verified from Weissenberg intensity data, and a refinement has been carried out yielding the following results. Each layer has the composition YAl$_3$, and the layer sequence is $\cdots ABABCBCAC \cdots$ or $\cdots chhchhchh \cdots$ to indicate whether the immediate surroundings are of the h.c.p. or the c.c.p. type.

The space group is $R\bar{3}m$ (No. 166) with 36 atoms per hexagonal unit cell.

$(0, 0, 0;\ \tfrac{1}{3}, \tfrac{2}{3}, \tfrac{2}{3};\ \tfrac{2}{3}, \tfrac{1}{3}, \tfrac{1}{3})+$

3 Y(1) in (a): $0, 0, 0$

6 Y(2) in (c): $0, 0, z;\ 0, 0, \bar{z}$ with $z=0{\cdot}2180\pm0{\cdot}0003$

9 Al(1) in (e): $\tfrac{1}{2}, 0, 0;\ 0, \tfrac{1}{2}, 0;\ \tfrac{1}{2}, \tfrac{1}{2}, 0$

18 Al(2) in (h): $x, \bar{x}, z;\ x, 2x, z;\ 2\bar{x}, \bar{x}, z$

$\bar{x}, x, \bar{z};\ \bar{x}, 2\bar{x}, \bar{z};\ 2x, x, \bar{z}$

with $x=0{\cdot}4785\pm0{\cdot}0006$ and $z=\tfrac{2}{9}$

The temperature factors are: B(Y)$=1{\cdot}1\pm0{\cdot}1$ Å^2 and B(Al)$=1{\cdot}8\pm0{\cdot}4$ Å^2. Some of the atomic positional parameters deviate significantly from the ideal values for close packing of equal spheres, that is $z_{\rm Y}=2/9=0{\cdot}2222$ and $x_{\rm Al}=\tfrac{1}{2}$. The value of $z_{\rm Al}$, however, remains unchanged within the accuracy of the refinement. This was carried out for 212 independent reflexions, using a least-squares program (Åsbrink & Brändén, 1962) available at this Institute. The program treats only orthorhombic and lower symmetries, and thus the errors computed for the structural parameters should not be taken as true standard deviations. Their order of magnitude ought to be correct, however. The final R value obtained was 0·114. No attempt was made to refine anisotropic thermal parameters. A more detailed report also containing structure factors and powder data, will be given in *Acta Chem. Scand.*

The atomic positions in a c.c.p. layer and in an h.c.p. layer are represented in Fig. 1. Interatomic distances are summarized in Table 1. There are no Y–Y contacts in the structure.

Table 1. *Interatomic distances in* YAl_3

Atom	Neighbour	Number of neighbours	Distance
Y(1)	Al(1)	6	$3{\cdot}09_8$ Å
Y(1)	Al(2)	6	3.09_7
Y(2)	Al(1)	3	$3{\cdot}02_3$
Y(2)	Al(2)	3	$3{\cdot}03_0$
Y(2)	Al(2)	6	$3{\cdot}10_7$
Al(1)	Al(1)	4	$3{\cdot}09_8$
Al(1)	Al(2)	4	$2{\cdot}88_9$
Al(1)	Y(1)	2	$3{\cdot}09_8$
Al(1)	Y(2)	2	$3{\cdot}02_3$
Al(2)	Al(1)	2	$2{\cdot}88_9$
Al(2)	Al(2)	2	$3{\cdot}49_8$
Al(2)	Al(2)	2	$2{\cdot}69_7$
Al(2)	Al(2)	2	$2{\cdot}81_8$
Al(2)	Y(1)	1	$3{\cdot}09_7$
Al(2)	Y(2)	1	$3{\cdot}03_0$
Al(2)	Y(2)	2	$3{\cdot}10_7$

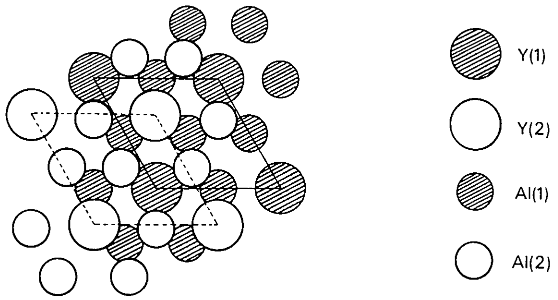

Fig. 1. Two superposed YAl_3 layers.
Open circles: h.c.p. layer $z_{Al}=0{\cdot}111$ $z_Y=0{\cdot}115$.
Filled circles: c.c.p. layer $z_{Al}=z_Y=0$.
The Al(2) positions deviate from ideal h.c.p. positions which are at the centres of the broken lines.

The c.c.p. layers at $z=0$, $z=\frac{1}{3}$ and $z=\frac{2}{3}$ are exactly planar, subject to space group requirements. The arrangement of Al(1) around Y(1) in these layers is perfectly hexagonal, resulting in a rather long Al(1)–Al(1) distance, equal to the Y(1)–Al(1) distance.

The aluminum structure of the h.c.p. layers is planar. These layers occur at $z=\frac{1}{9}$, $z=\frac{2}{9}$, $z=\frac{4}{9}$ *etc.* within the accuracy of the refinement. An yttrium atom in such a layer is displaced toward the neighboring h.c.p. layer where the contacting aluminum triangle is expanded, the Al(2)–Al(2) distance being 3·50 Å. Remaining Al(2)–Al(2) distances within the h.c.p. layer are short, 2·70 Å, in comparison with the contact distance, 2·86 Å, in the pure element.

The coordination of Al around Y(1) is quite regular, all twelve Y–Al distances being equal to 3·10 Å.

Around Y(2) there are six long, 3·11 Å, Y(2)–Al(2) contacts within the h.c.p. layer. The remaining six Y(2)–Al distances, of which three are Y(2)–Al(1) and three Y(2)–Al(2) are short and approximately equal, ~3·03 Å. The mean Y(2)–Al distance is 3·07 Å.

A recent article, (Runnalls & Boucher, 1965) reports a partial refinement of the structure of $PuAl_3$, which is isostructural with YAl_3. In that work, $z_{Pu}=0{\cdot}2185$ is given, which indicates that the deviation from ideal close packing of equal spheres is of the same type in the two phases. In $PuAl_3$, however, the h.c.p. Al layers have been assumed to be displaced from the ideal z (1/9, 2/9 *etc.*) so as to produce equal distortions of the coordination around Pu(1) and Pu(2).

The same structure type has been observed (Giessen & Grant, 1965) for $Ta(Pd_{0{\cdot}88}Ru_{0{\cdot}12})_3$ and $Ta(Pd_{0{\cdot}72}Rh_{0{\cdot}28})_3$. No refinement of these structures has apparently been reported.

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References

Bruzzone, G. & Ferro Ruggiero, A. (1962). *Rendiconti*, **33**, 465.
Giessen, B. C. & Grant, N. J. (1965). *Acta Cryst.* **18**, 1080.
Runnals, O. J. C. & Boucher, R. R. (1965). *Acta Cryst.* **19**, 184.
Vucht, J. H. N. van & Buschow, K. H. J. (1964). *Philips Res. Repts.* **19**, 319.

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Über trigonale Doppelselenate.

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Die Anhydrate der Alaune kristallisieren meist trigonal, wahrscheinliche Raumgruppe $P321$ (D_3^2), Zahl der Formeleinheiten in der Elementarzelle = 1 (Vegard & Maurstad, 1928; Franke & Henning, 1965.) Entsprechende Doppelselenate wurden bisher noch nicht untersucht. Die allgemeine Formel lautet: $A^+B^{3+}(SeO_4)_2$ (mit A : Cs, Rb, Tl, NH_4, K und B: Al, Ga, Cr, Fe, In.)

Die den angegebenen Kationenkombinationen entsprechenden Verbindungen wurden durch thermischen Abbau der Alaune dargestellt. Wasserfreie Doppelselenate, deren zugehörige Alaune nicht existieren, wurden durch Eindunsten einer Lösung der jeweiligen Zusammensetzung bei 5 °C und Tempern des Rückstandes bei 150 °C gewonnen.

Alle Chromverbindungen waren röntgenamorph, bei Erhöhung der Abbautemperatur zersetzten sie sich.

Die Pulverdiagramme (Zählrohrdiffraktometer, Cu $K\alpha$-, bzw. Fe $K\alpha$-Strahlung) der in Tabelle 1 aufgeführten Substanzen liessen sich einwandfrei trigonal indizieren. Ein Vergleich der Intensitätsverhältnisse und Gitterdaten zeigt, dass Doppelsulfate und Doppelselenate isotyp sind.