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The crystal structure of Zr_3Al_2.

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The crystal structure of the intermetallic compound Zr_3Al_2 has been determined from single-crystal and powder photographs. The alloy was prepared by arc welding in argon by Miss J. Murray, of A.E.R.E., Harwell. Powder specimens were obtained by filing a small solid sample which had been annealed for two weeks at 1100 °C. and quenched. Very small single crystals were selected under a microscope from the debris obtained by crushing part of the same specimen. The symmetry and the unit-cell dimensions were determined from single-crystal oscillation and rotation photographs, and the tetragonal symmetry was confirmed by Laue photographs taken along the axes of the crystal. A more accurate determination of the unit cell was made using powder photographs taken with a precision 19 cm. camera (Adam, 1954) and Cu $K\alpha$ radiation. Measurement of the powder photographs was difficult owing to an appreciable background caused by fluorescent Zr K radiation excited by the continuous spectrum of the copper target. (The fluorescent background was reduced to a minimum by operating the X-ray set at 18 kV.). Fairly accurate line spacings were obtained by taking several independent readings of the films with an illuminated-fibre measuring device. The values of $\sin^2\theta$ obtained from these measurements and the visual estimate of line intensities are given in Table 1.

Table 1. *X-ray data*

hkl	Observed $\sin^2\theta$	Calculated $\sin^2\theta$	Observed intensity	Calculated intensity
110	*206	205	V_2W	5·6
002	*479	487	V_2W	2·8
210	515	511	M	41
112	694	691	MW	47
220	823	818	M	55
202	898	895	S	148
221	943	939	V_3W	10·6
212	1000	997	S	148
310	*1024	1022	S	112
311	1146	1143	VW	25
113	*1287	1298	V_2W	3·2
320	1326	1328	V_3W	9·3
321	1441	1450	V_4W	2·7
312	1511	1508	V_4W	7·8
410	1736	1737	M	40
004	1943	1944	MW	39
420	2045	2043	V_2W	14·4
402	2120	2120	VW	8·3
412	2222	2222	M	59
332	2325	2325	M	66
323	*2425	2421	VW	1·1
214	2460	2455	V_2W	27
422	2531	2529	V_3W	20
510	*2656	2656	VW	7·0
224	2761	2760	W	33
413	2831	2830	V_4W	9·6
333	*2926	2932	V_3W	2·6
520	2965	2962	MS	1·8
314		2966		68
521	3087	3084	V_3W	7·9
423	3141	3137	MW	0·3
512		3141		52
105		3138		2·4

S = strong; M = medium; MW = medium weak; MS = medium strong; W = weak; VW = very weak; V_2W, V_3W and V_4W = decreasing weak.

Metallographic examination of an etched and polished surface of the bulk specimen showed that the alloy specimen was not a pure single phase. The specimen micrograph showed a structure of primary crystals and an appreciable amount of what appeared to be a eutectic. The powder films contained a large number of lines which were shown to belong to the neighbouring phase Zr_4Al_3 whose structure is known (Wilson, Thomas & Spooner, 1960). In addition there were a few very weak lines of the neighbouring phase Zr_5Al_3. It is presumed that these two impurity phases formed the 'eutectic' observed under the microscope. It is interesting to note that Debye–Scherrer films taken of the same powder which had been annealed in vacuo at 700 °C. for two weeks appeared to consist mainly of Zr_4Al_3 with a smaller quantity of Zr_5Al_3. The lines marked in Table 1 refer to the identified Zr_4Al_3 and Zr_5Al_3, phases.

All the lines belonging to Zr_3Al_2 have been indexed on a tetragonal unit cell with:

$$a = 7{\cdot}630 \pm 0{\cdot}001,\quad c = 6{\cdot}998 \pm 0{\cdot}001\ \text{Å}\ .$$

These values for the cell dimensions and the calculated values of $\sin^2\theta$ shown in Table 1 have been obtained by using a Nelson–Riley extrapolation method.

The calculated density on the basis of $4\{Zr_3Al_2\}$ in the unit cell is 5·34 g.cm.$^{-3}$, compared with the value 5·35 g.cm.$^{-3}$, determined with a specific-gravity bottle.

From the indices of the reflections obtained with the single crystal photographs the systematic absences observed were $00l$, $l = 2n$ and $h0l$, $h+l = 2n$, which led to space group D_{4h}^{14}–$P4_2/mnm$ being selected. The calculated line intensities given in Table 1 were obtained with the atoms in the following positions:

8 Al (j) x, x, z; with $x = \frac{1}{8}$, $z = 0{\cdot}21$
4 Zr (f) $x, x, 0$; with $x = 0{\cdot}34$
4 Zr (g) $x, x, 0$; with $x = 0{\cdot}20$
4 Zr (d) $0, \frac{1}{2}, \frac{1}{4}$.

The single crystals used were too irregular in shape to allow a suitable absorption correction to be determined for the intensities of the oscillation photographs. An absorption correction factor was calculated for the powder line intensities by determining the average density of the powder specimens and using the known atomic absorption coefficients of zirconium and aluminium. This correction factor is included in the calculated line intensities given in Table 1.

The agreement between observed and calculated line intensities given in Table 1 is good, most discrepancies being accounted for by overlapping lines from the neighbouring phases. For larger reflection angles the visual estimate of line intensities is not sufficiently good to allow a direct comparison with calculated line intensities owing to the lack of film contrast caused by the increasing zirconium fluorescence. However, the overall agreement between observed and calculated intensities is satisfactory when neighbouring lines within any group of lines are compared. Because of the lack of precision in the visual estimates no R factors are given in Table 1.

The four variable atomic parameters were chosen by trial and error to give the best intensity agreement, more weight being given to the small-angle lines. It was found that the atoms could be moved slightly from their present positions without seriously affecting the intensity agreement. It is apparent that the powder method adopted for this investigation is not sufficiently good to give high accuracy and because of this it was decided to abandon any further refinement of the structure. Assuming an uncertainty of ±0·005 in the atomic parameters gives rise to the errors indicated in the following table of interatomic distances:

(4) Zr–Zr = 3·36 ± 0·04 Å
(4) Zr–Zr = 3·36 ± 0·05
(2) Al–Zr = 3·03 ± 0·06
(2) Al–Zr = 2·99 ± 0·10
(1) Al–Zr = 2·77 ± 0·11 Å
(1) Al–Zr = 2·75 ± 0·07
(1) Al–Al = 2·70 ± 0·11

Discussion

The crystal structure of Zr_3Al_2 was at first thought to be isomorphous with Hg_3Na_2, but packing considerations and intensity discrepancies do not allow Zr atoms to occupy the $(0, \frac{1}{2}, 0)$ positions occupied by Hg atoms in Hg_3Na_2. Good intensity agreement and good packing were achieved by putting these atoms in the $(0, \frac{1}{2}, \frac{1}{4})$ positions of the Hg_3Na_2 structure.

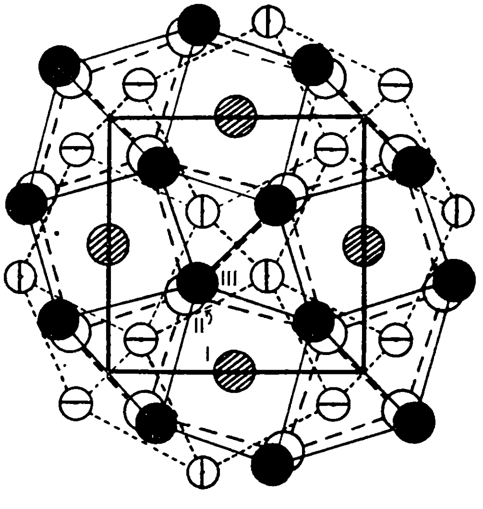

Fig. 1.

◍ : Zr atoms; $z = \frac{1}{4}$. ● : Zr atoms; $z = \frac{1}{2}$. ○ : Zr atoms; $z = 0$. ⦶ : Al atoms; $z = 0·21$. ⊖ : Al atoms; $z = 0·29$.

It is interesting to discuss the proposed structure in the light of the findings of Frank & Kasper (Frank & Kasper, 1958, 1959). The Zr atoms in the (f) and (g) positions form two plane layers, the atoms in each plane being arranged in slightly dissimilar distorted square-triangle nets having the Schläfi symbols $3^2.4.3.4$. The Zr atoms in the (d) positions also lie in plane layers at $z = \frac{1}{4}$ and $z = \frac{3}{4}$ and, as shown in the projection of the cell in the x–y plane in Fig. 1, form a square net which is part of the 'in-filling' of the distorted square-triangle nets. The Al atoms which lie in the remaining 'holes' of the square-triangle nets form a net whose projection is an undistorted square-triangle net. Since the Al atoms lie slightly above and below the Zr atoms in the $z = \frac{1}{4}$ planes they might be regarded as part of the complete in-filling which is a puckered layer of Zr and Al atoms.

The half-cell shown in the projection in Fig. 1 bears some resemblance to the unit cell of tetragonal $CuAl_2$. It would be exactly similar if (i) the two Zr square-triangle nets were undistorted similar layers; (ii) all the Al atoms were in the $z = \frac{1}{4}$ planes and (iii) the square Zr net lay at $z = \frac{1}{8}$ instead of $z = \frac{1}{4}$. Because of the difference in size between the Zr and Al atoms it is not possible to produce a $CuAl_2$ type of structure or a modification of this in which all the Al atoms and some Zr atoms lie symmetrically between two undistorted and superimposed square-triangle nets of Zr atoms without packing difficulties. In any case such a cell would be half the height of the present cell and this is not borne out by the single-crystal photographs.

All the atoms in the proposed structure have triangulated co-ordination shells. The co-ordination number (as defined unambiguously by Frank & Kasper) of the Zr atoms designated I, II and III in Fig. 1, are 14, 14 and 15, respectively, whilst the co-ordination number of each Al atom is 12. The Zr(I) atoms lie in vertical rows whilst Zr(II) and Zr(III) lie in 'crinkled' vertical rows. Apart from the fact that the co-ordination shells of the Zr(I) and Zr(II) atoms are somewhat prolate rather than oblate the structure thus conforms to the principle of sphere packing in complex alloy structures as enunciated by Frank & Kasper.

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References

Adam, J. (1954). *J. Sci. Instrum.* **31**, 131.
Frank, F. C. & Kasper, J. S. (1958). *Acta Cryst.* **11**, 184.
Frank, F. C. & Kasper, J. S. (1959). *Acta Cryst.* **12**, 483.
Wilson, C. G., Thomas, D. K. & Spooner, F. J. (1960). *Acta Cryst.* **13**, 56.