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The Crystal Structure of $ZrAl_2$

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The crystal structure of $ZrAl_2$ has been determined from powder samples and imperfect single crystals. The unit cell is hexagonal with

$$a = 5\cdot282,\quad c = 8\cdot748\ \text{Å};\quad c/a = 1\cdot656\ .$$

There are four $ZrAl_2$ units per cell. The calculated density is 4·56 g.cm.$^{-3}$. The space group is $P6_3/mmc$. The structure is a Laves phase of the C_{14}, $MgZn_2$ type. The contraction of the Al substructure and the expansion of the Zr substructure support the general conclusions about the constitution of Laves phases.

McPherson & Hanson (1954) have published the equilibrium diagram for zirconium–aluminium and reported that the intermetallic compound $ZrAl_2$ has an orthorhombic unit cell with

$$a = 10\cdot42,\quad b = 7\cdot22,\quad c = 4\cdot98\ \text{Å}\ .$$

In order to investigate this structure more fully a sample of the alloy was prepared by arc-melting in argon and given to this laboratory by Miss J. R. Murray, A.E.R.E., Harwell. Micrographs taken from a polished and etched section showed that the sample was approximately single phase, the maximum grain size being about 0·3 mm. The impurity phase, which was estimated to be present in the approximate ratio 1:17. was later identified as the intermetallic compound Zr_2Al_3. Both Debye–Scherrer powder photographs and single-crystal (rotation and oscillation) photographs were used.

For the Debye–Scherrer films a precision camera of 19 cm. diameter (Adam, 1954) was kindly lent by Dr J. Adam, A.E.R.E., Harwell. The powder specimen was prepared by crushing and grinding with an agate mortar so as to pass through a 300 × sieve and inserted in a 0·3 mm. radius Lindemann-glass tube. The $ZrAl_2$ alloy is very brittle and the sharpness of the diffraction lines indicated that annealing of the powder was not necessary. All the films were taken with filtered Cu $K\alpha$ radiation. The diffraction lines were measured with an illuminated fibre device similar to that of Lees (1955) with an accuracy of $\pm 0\cdot005$ cm. This instrument gave much better reproducibility of readings on the weak and very weak lines than was possible with a precision travelling microscope.

From the calculated values of $\sin^2\theta$ it was found that all the lines could be indexed on a hexagonal unit cell with

$$a = 5\cdot2824 \pm 0\cdot0005,\quad c = 8\cdot7482 \pm 0\cdot0005\ \text{Å}\ ,$$
$$c/a = 1\cdot656\ .$$

An extrapolation method using the Nelson–Riley function was used to obtain accurate cell dimensions. Confirmation of this unit cell was obtained by using very small and somewhat imperfect single crystals produced by crushing a piece of the specimen. Rotation and oscillation photographs were taken with both

Table 1. *X-ray data*

hkl	$\sin^2\theta\times10^4$ (obs.)	$\sin^2\theta\times10^4$ (calc.)	Intensity (visual)	Intensity (calc.)
$10\bar{1}0$	289	287	*w*	10
0002	315	315	*vw*	6
$10\bar{1}1$	367	366	*w*	8
$10\bar{1}2$	601	601	*m*−	10
$11\bar{2}0$	859	858	*s*	40
$10\bar{1}3$	992	990	*vs*	62
$20\bar{2}0$	1143	1143	*m*−	9
$11\bar{2}2$	1170	1170	*vs*	61
$20\bar{2}1$	1220	1221	*m*	32
0004	1250	1251	*vvw*	3
$10\bar{1}4$	1535	1535	*vvw*	2
$20\bar{2}3$	1843	1844	*w*	6
$21\bar{3}0$	1995	1996	*vw*	2
$21\bar{3}1$	2071	2075	*vw*	3
$10\bar{1}5$	2232	2235	*m*−	13
$21\bar{3}2$	2306	2307	*vw*	4
$30\bar{3}0$	2562	2565	*m*−	12
$21\bar{3}3$	2694	2696	*s*	40
0006	2806	2806	*vvw*	4
$30\bar{3}2$	2872	2871	*m*	21
$20\bar{2}5$ $10\bar{1}6$	3083	3082 3085	*m*	32
$21\bar{3}4$	3237	3235	*vvw*	2
$22\bar{4}0$	3413	3410	*m*	22
$11\bar{2}6$	3654	3652	*vvw*	2
$22\bar{4}2$	3724	3721	*vvw*	3
$21\bar{3}5$ $20\bar{2}6$	3935	3932 3935	*m*	22
$31\bar{4}2$	4003	4005	*vw*	2
$10\bar{1}7$	4096	4092	*vvw*	3
$31\bar{4}3$	4392	4392	*m*	24
$40\bar{4}0$	4548	4544	*vvw*	2
$40\bar{4}1$	4622	4622	*vw*	7
$21\bar{3}6$	4783	4784	*vvw*	5
$40\bar{4}3$ $10\bar{1}8$	5249	5242 5254	*vw*	9
$30\bar{3}6$	5351	5351	*vvw*	2
$31\bar{4}5$	5631	5631	*w*	12

Table 1 (*cont.*)

hkl	$\sin^2\theta\times10^4$ (obs.)	$\sin^2\theta\times10^4$ (calc.)	Intensity (visual)	Intensity (calc.)
$40\bar{4}4$ $21\bar{3}7$	5789	5784 5791	*vvw*	5
$11\bar{2}8$	5820	5821	*m*−	13
$41\bar{5}0$	5962	5961	*m*−	13
$32\bar{5}3$ $20\bar{2}8$	6092	6091 6092	*m*−	25
$22\bar{4}6$	6202	6200	*m*−	13
$41\bar{5}2$	6271	6270	*m*	26
$40\bar{4}5$	6483	6481	*m*	16
$10\bar{1}9$	6569	6570	*vvw*	3
$21\bar{3}8$	6953	6953	*m*−	15
$32\bar{5}5$	7332	7330	*m*−	15
$30\bar{3}8$	7518	7518	*m*−	17
$33\bar{6}0$	7660	7659	*w*	9
$50\bar{5}3$	7789	7789	*m*−	15
$42\bar{6}0$	7938	7942	*vvw*	6
$33\bar{6}2$	7970	7969	*m*−	18
$42\bar{6}1$	8016	8019	*m*−	17
$32\bar{5}6$	8183	8181	*w*	7
$21\bar{3}9$	8268	8268	*w*	8
$22\bar{4}8$	8368	8367	*vvw*	5
$42\bar{6}3$ $31\bar{4}8$	8647	8638 8650	*m*	34
$41\bar{5}6$	8747	8747	*m*−	11
$2,0,\bar{4},10$	8889	8889	*w*	13
$50\bar{5}5$	9028	9027	*m*−	14
$32\bar{5}7$	9188	9187	*w*	13
$51\bar{6}3$	9487	9487	*vs*	74
$1,0,\bar{1},11$	9665	9665	*m*	27

vvw = very very weak, *vw* = very weak, *w* = weak, *m*− = medium weak, *m* = medium strong, *s* = strong, *vs* = very strong.

All $\sin^2\theta$ values below dotted line refer to resolved α_1 components.

a and c as axes of rotation. The observed and calculated values of $\sin^2\theta$ are given in Table 1.

Using the atomic volumes of the zirconium and aluminium atoms derived from the elementary crystalline forms, the proposed unit cell contains four units of $ZrAl_2$. The calculated density was 4·56 g.cm.$^{-3}$; the density determined experimentally, using a bulk sample containing the impurity phase, was 4·42 g.cm.$^{-3}$.

The visually estimated and calculated line intensities are given in Table 1. The calculated intensities were corrected for absorption but the temperature factor was ignored. The absorption factor was obtained from a table given in Klug & Alexander (1954) for cylindrical powder specimens. The value of $\mu r = 3{\cdot}1$, used for this purpose, was based on a calculated composite absorption coefficient for the compound and an experimentally determined powder density.

The single-crystal photographs indicated the following conditions for reflection: $(000l)$, $l=2n$; $(hh\overline{2h}l)$, $l=2n$; $(hkil)$, for $h-k=3n$, $l=2n$. Although several space groups are possible a good intensity agreement was found using $P6_3/mmc$ with the atoms in the following positions:

4 Zr in (f) positions: $\frac{1}{3}, \frac{2}{3}, z$; $z=\frac{1}{16}$
6 Al in (h) positions: $x, 2x, \frac{1}{4}$; $x=-\frac{1}{6}$
2 Al in (b) positions: 0, 0, 0.

No attempt was made to refine the Zr and the Al parameters. The proposed $ZrAl_2$ structure is thus a Laves phase of the C_{14}, $MgZn_2$ type. The interatomic distances are given in Table 2.

Table 2. *Interatomic distances*

Zr–Zr: 2 at 3·28 and 2 at 3·24 Å
Al–Al: 6 at 2·67 and 2 at 2·64 Å
Zr–Al: 1 at 3·13, 1 at 3·11 Å and 1 at 3·08 Å

Discussion

In the ideal Laves phase of the C_{14} type which is formed when $c/a = (8/3)^{\frac{1}{2}} = 1{\cdot}633$, the B atoms occupy corners of regular tetrahedra which are joined alternately point to point and base to base. The larger A atoms occupy the 'holes' formed by the tetrahedra to form another substructure which is characteristic of the phase. Any departure from $c/a = (8/3)^{\frac{1}{2}}$, leads to a change in the height of the B tetrahedra and consequent small differences in the interatomic distances in each substructure as observed in Table 2.

The important parameter governing the formation of Laves phases, when the c/a ratio is approximately correct, is the ratio of the atomic diameters of the two components d_A/d_B. In the ideal C_{14} structure, in which A atoms touch each other and B atoms touch each other, $d_A/d_B = (1{\cdot}5)^{\frac{1}{2}} = 1{\cdot}225$. Berry & Raynor (1953) showed that if $W = d_A/d_B$ is less than 1·225, there should be a contraction of the B substructure and an expansion of the A substructure. Assuming the atomic diameters d_A and d_B to be the interatomic distances in pure metallic zirconium and aluminium, 3·17 and 2·862 Å respectively, we find for $ZrAl_2$ that $W = 1{\cdot}108$. Although this is a rather low value there are at least two other compounds, *viz.* WFe_2 and $MnBe_2$, for which W is smaller. On the other hand, it is interesting to note that there is no Laves phase of the C_{14} type with Al as the B atom reported in the list given by Berry & Raynor. The expected contraction of the B substructure and the expansion of the A substructure is clearly revealed by the interatomic distances given in Table 2.

Following Berry & Raynor, and using the maximum interatomic distances listed in Table 2, the parameters S_{AA}, S_{BB} and S_{AB}, are determined for $ZrAl_2$. These parameters represent the percentage deviation from the interatomic distances in the pure components and are defined by the expressions:

$$S_{AA} = 100(d_{AA}-d_A)/d_A, \quad S_{BB} = 100(d_{BB}-d_B)/d_B\,,$$

$$S_{AB} = \frac{100\,[d_{AB}-\frac{1}{2}(d_A+d_B)]}{\frac{1}{2}(d_A+d_B)}\,.$$

For $ZrAl_2$: $S_{AA} = 3{\cdot}48\%$, $S_{BB} = -6{\cdot}84\%$ and $S_{AB} = 3{\cdot}79\%$. The values of S_{AA}, S_{BB} and S_{AB} for the known C_{14} Laves phases formed by zirconium as the A component are plotted against W in Fig. 1, to give a diagram similar to that first presented by Berry &

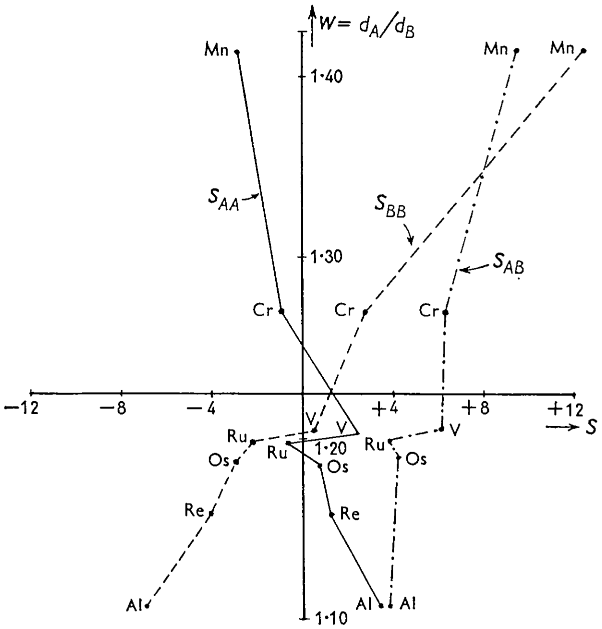

Fig. 1. Plot of S_{AA}, S_{BB} and S_{AB} against $W = d_A/d_B$ for Laves phases of the C_{14} type with zirconium as the '*A*' component.

———— S_{AA}; - - - - S_{BB}; —·—·— S_{AB}.

Raynor. Aluminium appears to fit very well into this scheme and since chemically aluminium differs considerably from all other metals in this set, the importance of geometrical factors in the formation of the C_{14} phase seem to be over-riding.

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References

Adam, J. (1954). *J. Sci. Instrum.* **31**, 131.
Berry, R. L. & Raynor, G. V. (1953). *Acta Cryst.* **6**, 178.
Klug, H. P. & Alexander, L. E. (1954). *X-ray Diffraction Procedures*, p. 155. New York: Wiley.
Lees, C. S. (1955). *J. Sci. Instrum.* **32**, 17.
McPherson, D. J. & Hanson, M. (1954). *Trans. Amer. Soc. Metals*, **46**, 354.

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Transition Element—Rare Earth Compounds with the Cu_5Ca Structure

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A number of new B_5A compounds, with A a rare earth or yttrium and B a transition element, Co, Ni, or Cu, having the Cu_5Ca structure, have been prepared. In most of the compounds, the interatomic distances are normal. However, Ce appears to have a valence substantially greater than three. Also, in Co_5Pr, Pr appears to have a valence slightly greater than three.

Introduction

In the course of a continuing study of the magnetic and structural properties of intermetallic compounds between rare earth and transition metals, a number of new compounds with the Cu_5Ca structure have been made. Some of the results of magnetic measurements have already been reported by Nesbitt *et al.* (1959). It is the purpose of this paper to report on the crystallographic investigations of these new compounds.

Experimental

Stoichiometric amounts of the constituents were melted by induction heating in fused Al_2O_3 or quartz crucibles in an argon atmosphere.* The compounds appear to melt congruently as they form readily from the melt.

X-ray powder photographs were taken with Cr $K\alpha$ radiation and a Straumanis type Norelco camera (114·6 mm. diameter). Observed and calculated interplanar spacings are shown in Table 1.

These compounds, B_5A, belong to space group $P6/mmm(D_{6h}^1)$ with A in (a): 0, 0, 0, $2B_{\rm I}$ in (c): $\pm(\frac{1}{3}, \frac{2}{3}, 0)$, and $3B_{\rm II}$ in (g): $\frac{1}{2}, 0, \frac{1}{2}$, $0, \frac{1}{2}, \frac{1}{2}$, $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$.

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* All of the rare earth elements, except Pr (99·9+%), and Y were of 99+% purity. Co and Ni 99·9+%; Cu 99·999%. The Nd was kindly supplied to us by Dr F. H. Spedding.