Acta Cryst. (1961). **14**, 469

The Crystal Structure of Zr_2Al_3

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(*Received* 12 *July* 1960)

The crystal structure of Zr_2Al_3 has been determined by Patterson and Fourier methods on a small single crystal. The crystal is orthorhombic with

$$a = 9{\cdot}601,\ b = 13{\cdot}906,\ c = 5{\cdot}57\ \text{Å}\ .$$

The space group is *Fdd*2, with eight formula weights per cell. The structure is described and illustrated with a drawing of the unit cell. The zirconium atoms each have a co-ordination group consisting of nine aluminium atoms and four other zirconium atoms. The aluminium atoms are of two kinds, but each kind possesses a co-ordination group consisting of six zirconium atoms and four aluminium atoms.

Introduction

In the report on the thermal equilibrium diagram of the zirconium aluminium system by McPherson & Hansen (1954), it is stated that a phase which might be represented by either of the formulae Zr_3Al_4 (28·27% wt. Al.) or Zr_2Al_3 (30·72% wt. Al.) is formed by a peritectic reaction between the phase $ZrAl_2$ (37·16% wt. Al.) and a melt containing about 30% aluminium at 1595 °C. The evidence then available suggested that the designation Zr_2Al_3 be tentatively adopted.

Experimental

The present specimen was prepared by Miss J. Murray of A.E.R.E., Harwell, by arc melting in argon. The aluminium used was Noral superpurity containing 99·999 + % Al and the zirconium was Murex sponge made by the Kroll process and probably contains 2% to 3% Hafnium. The melt contained 29·6% Al by weight and was received in the 'as cast' state.

The microstructure showed dendritic crystals of Zr_2Al_3 with an impurity precipitate. The impurity phase was estimated to be present in less than 1 part in 16, but it could not be identified with certainty.

A powder photograph was taken by Dr J. Adam, A.E.R.E., Harwell, with a Guinier type focusing camera using monochromatic Cu $K\alpha$ radiation. Using the method of de Wolff (1957) it was possible to index all but a few weak lines on the basis of a face-centred orthorhombic unit cell with

$$a = 9{\cdot}601 \pm 0{\cdot}002,\ b = 13{\cdot}906 \pm 0{\cdot}002,$$
$$c = 5{\cdot}574 \pm 0{\cdot}002\ \text{Å}\ .$$

Assuming this cell to contain eight units of Zr_2Al_3, the calculated density is 4·703 g.cm.$^{-3}$. The density of the specimen measured with a specific gravity bottle was 4·79 ± 0·06 g.cm.$^{-3}$.

Attempts to determine the structure from the powder data on a trial-and-error basis failed.

A near-single crystal whose dimensions were of the order of 0·2 mm. was found from the powder, and *hk*0, *hk*1, 0*kl* and *h*0*l* Weissenberg photographs were taken with a 5 cm. radius camera (Beevers, 1952) using Cu $K\alpha$ radiation. The cell dimensions were determined and found to be in agreement with those obtained from the powder data. The intensities were estimated visually using a calibrated scale. Examination of corresponding diffraction spots on the same film was carried out to determine whether the size and the mounting of the specimen produced any serious errors in the intensity of the spots.

A test for piezo-electricity carried out by the Giebe & Scheibe method suggested the presence of a centre of symmetry, but the space group found did not possess a centre of symmetry.

Determination and refinement of the structure

The systematic absences uniquely specify the space group as $Fdd2(C_{2v}^{19})$ [*hkl* reflexions present only when *h*, *k* and *l* are all even or all odd; 0*kl* and *h*0*l* reflexions present only when the sum of the indices = 4*n*.]

A Patterson projection down the *c* axis indicated that suitable *x* and *y* parameters would be 0·062 and 0·195 for one set of zirconium atoms lying in general positions. By a graphical method of super-position the Patterson projection indicated that there was a set of aluminium atoms in the general position with suitable

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parameters $x=0{\cdot}062$ and $y=0{\cdot}122$, and one set of aluminium atoms in the special position $x=0$, $y=0$.

A Patterson projection down the a axis indicated that, if the z co-ordinate is taken as 0 for the zirconium, the aluminium atoms in the general position had a z co-ordinate of 0·500. For the aluminium atoms in the special position the choice of $z=0{\cdot}125$ was consistent both with the Patterson projection and with packing considerations.

Table 1. *Positional parameters in* Zr_2Al_3

16 Zr atoms in (b) (x, y, z) with $x=0{\cdot}068$, $y=0{\cdot}196$, $z=0{\cdot}000$
16 Al atoms in (b) (x, y, z) with $x=0{\cdot}065$, $y=0{\cdot}116$, $z=0{\cdot}500$
8 Al atoms in (a) $(0, 0, z)$ with $z=0{\cdot}125$

Comparisons of the $hk0$ structure factors with the observed intensities furnished an R factor of 22%. (F_o-F_c) difference Fourier syntheses were prepared and from the map slight shifts were indicated. With the zirconium atoms placed at $x=0{\cdot}068$ and $y=0{\cdot}196$, and the aluminium atoms at $x=0{\cdot}065$ and $y=0{\cdot}116$, the R factor for this projection dropped to 17·6%.

Consideration of the $0kl$ structure factors after this adjustment showed an R factor of 18·7%.

Four cycles of refinement of the structure were carried out on the $(00l)$ projection since in this synthesis no overlap of peaks occurs. No attempt was made to refine beyond a parameter interval of 0·001 for zirconium or 0·002 for aluminium, and no temperature factor was applied.

Discussion of the structure

Fig. 1 is a projection of the unit cell down the short ($c=5{\cdot}57$ Å) axis, the Zr atoms being shown as the larger circles and the Al atoms as the smaller circles. The z co-ordinates are shown in Å as numbers either within or adjacent to the various atoms. The space group $Fdd2$ is of interest in that the two d glide planes are the only necessary elements of symmetry, one glide plane being perpendicular to the x axis and with a translation of $\frac{1}{4}(\mathbf{b}+\mathbf{c})$, and the other perpendicular to the y axis with a translation $\frac{1}{4}(\mathbf{a}+\mathbf{c})$. Two successive operations by one of the d glide planes will produce the face-centering of the cell. An operation of one glide plane followed by an operation of the other produces either the screw axes parallel to z or the rotation axes parallel to z in the positions shown in Fig. 1. In the

Table 2. *Comparison of observed and calculated structure factors and phase angles*

hkl	F_o	F_c	α
040	33	38	0
080	148	210	180
0,12,0	172	232	180
0,16,0	204	273	0
220	242	180	180
240	357	354	0
260	183	171	0
280	199	178	0
2,10,0	323	329	0
2,12,0	245	246	180
2,14,0	70	7	180
2,16,0	161	119	180
400	11	5	180
420	470	432	180
440	94	60	0
460	285	250	180
480	107	95	0
4,10,0	59	4	180
4,12,0	62	75	0
4,14,0	376	346	0
4,16,0	32	9	0
620	320	310	0
640	204	187	0
660	54	56	180
680	126	105	0
6,10,0	253	255	180
6,12,0	164	166	180
6,14,0	54	86	0
800	255	387	180
820	65	71	0
840	54	75	0
860	65	69	0
880	263	242	0
8,10,0	72	12	180
8,12,0	234	253	0
10,2,0	137	136	0
10,4,0	225	250	180
10,6,0	43	3	180
10,8,0	129	133	180
10,10,0	81	99	180
12,0,0	91	158	0
12,2,0	137	217	0
12,4,0	43	45	0
	$R=17{\cdot}6\%$		
040	35	38	0
080	159	210	180
0,12,0	202	232	180
0,16,0	220	273	0
022	459	382	169
062	168	164	23
0,10,2	468	406	8
0,14,2	58	80	149
004	318	433	0
044	58	82	180
084	274	263	180
0,12,4	347	274	180
026	263	230	190
066	147	111	340
	$R=18{\cdot}7\%$		
004	269	433	0
202	395	415	10
206	358	253	351
400	0	5	180
404	173	106	180
602	398	388	172
606	308	283	187
800	267	384	180
804	456	397	180
10,0,2	228	173	167
12,0,0	141	156	0
	$R=21{\cdot}2\%$		
111	210	131	298
131	263	161	238
151	452	463	324
171	260	242	176
191	144	149	43
1,11,1	179	216	74
1,13,1	82	118	98
1,15,1	201	220	53
1,17,1	116	102	162
311	427	344	121
331	386	320	44
351	170	196	67
371	233	227	222
391	235	214	325
3,11,1	98	118	277
511	174	131	242
531	224	238	7
551	170	134	111
571	250	320	104
591	216	282	30
5,11,1	107	151	146
711	120	81	118
731	188	236	338
751	230	258	190
771	226	232	316
911	122	166	35
931	145	101	84
951	145	174	122
971	154	192	18
	$R=17{\cdot}7\%$		

Notes: (1) Overall $R=18{\cdot}4\%$.
(2) The $h00$, $0k0$ and $00l$ intensities occur twice in the above table, the differences in the F_o values are due to errors in observations and to different scaling factors.

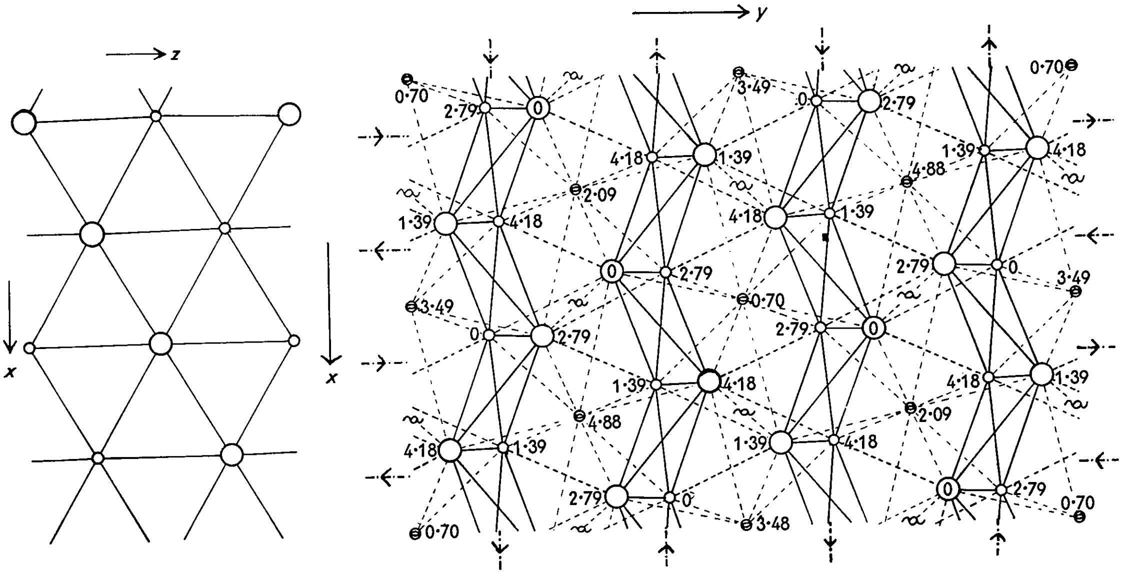

Fig. 1. On the right is a projection of the structure down the z axis, x and y axes being as shown. On the left is a projection down the y axis of the puckered triangular net which is arranged about the d glide plane at $y=\frac{1}{8}$. Zr atoms are shown as large circles and Al atoms as small circles, and the heights (z co-ordinates) of the atoms are shown in Å.

figure the two sets of glide planes are shown by the usual dot-and-dashed lines around the margin of the figure, the arrow heads on these lines indicating the direction of movement in the plane of the figure for an upward z displacement. The arrow heads on successive members of a family of glide planes are in opposite directions.

In order to obtain the structure of Zr_2Al_3 we must insert in this space group three atoms, the general Zr atom, the general Al atom and the special Al atom (on one of the two-fold axes). The general (16-fold) Zr atom has been placed at the position with co-ordinates (0·654, 2·73, 0) Å (near the top left hand corner of Fig. 1). It is thus at a distance of $2{\cdot}73-b/8=0{\cdot}99$ Å from the nearest glide plane perpendicular to y, and it is of course operated on by this glide plane which translates it a distance of $\frac{1}{4}(\mathbf{a}+\mathbf{c})=2{\cdot}77$ Å. The total distance between successive Zr atoms connected by this glide plane is thus $(2{\cdot}77^2+1{\cdot}98^2)^{\frac{1}{2}}=3{\cdot}40$ Å, a distance which can be regarded as a contact. The zig-zag line of Zr atoms thus produced by the glide plane is represented by full lines in Fig. 1.

The general Al atom with parameters (0·065, 0·116, 0·500) is only 0·13 Å from the same d glide plane perpendicular to y, so that this atom is also operated on to give a zig-zag line of atoms, in this case, however, very nearly straight, the Al–Al distance being very nearly 2·77 Å. This distance is also a contact, being a little smaller than the Al–Al distance of 2·86 Å in metallic Al itself. The two zig-zag lines of atoms form a puckered triangular net which is shown in elevation (face-on) at the left-hand side of Fig. 1, and is shown edge-on by the full lines in the z-axis projection in the main part of the figure. Thus within the puckered triangular net each Zr atom is in contact with two other Zr atoms and with four Al atoms, and each Al atom is in contact with two other Al atoms and four Zr atoms. The departure from planarity is evidently due to the difference in the size of the two metallic ions, the Al radius being about 1·43 Å and the Zr radius about 1·59 Å. The puckered triangular nets do not possess three-fold symmetry, although they would do so if the two kinds of atoms were identical, and this pseudo-symmetry is shown in the cell dimensions, since half the a–c face-diagonal is 5·551 Å and the angle this diagonal makes with the c axis (5·574 Å) is 59° 41′.

The puckered triangular nets are repeated in the y axis direction, and this repetition can be effected either by the d glide plane perpendicular to x or by the two-fold axes and screw axes. On the two-fold axes lie the special Al atoms. Each Zr atom makes contact with two of the special Al atoms on one side and with one special Al atom on the other. Also each Zr touches two Al atoms in a neighbouring net, and it is furthermore at 3·43 Å from two Zr atoms related to it by a screw axis, thus giving Zr a total co-ordination of thirteen. Each general Al atom not only has its six contacts within the puckered triangular net but makes two contacts with Zr atoms (one on each side of the net) and two contacts with special Al atoms (again one on each side of the net). This gives the general Al atom a co-ordination group of ten. The special Al atom has five pairs of contacts with three pairs of Zr atoms and two pairs of general Al atoms, although the distance to one pair of Zr atoms is 3·22 Å, considerably greater than the other distances (of 2·8 and 2·9 Å). All these interatomic distances are shown in Table 3 and there are no other distances in the structure below 3·8 Å.

Table 3. *Interatomic distances in* Zr_2Al_3

Distances in the Zr co-ordination polyhedron (13 atoms) (Å)

Zr–Al (*a*): 2·83, 2·89, 3·22
Zr–Al (*b*): 2·88, 2·91, 2·93, 2·97, 3·00 (twice)
Zr–Zr: 3·40 (twice), 3·43 (twice)

Distances in the general Al co-ordination polyhedron (10 atoms) (Å)

Al–Al (*a*): 2·67, 2·71
Al–Al (*b*): 2·77 (twice)
Al–Zr: 2·88, 2·91, 2·93, 2·97, 3·00 (twice)

Distances in the special Al co-ordination polyhedron (10 atoms) (Å)

Al–Al (*b*): 2·67 (twice), 2·71 (twice)
Al–Zr: 2·83 (twice), 2·89 (twice), 3·22 (twice)

The co-ordination polyhedra do not have any simple form. Their shapes can be obtained from the bonding shown in Fig. 1, where contacts outside the puckered triangular nets are shown as dotted lines and the bonds within the nets are shown as full lines.

No simple relation has been found between the structure of Zr_2Al_3 and that of $ZrAl_2$ (Wilson, 1959). The basic symmetry operations in the two structures are different, and, although there is a three-fold net in $ZrAl_2$ also, it is made up of Al atoms forming a planar 4-connected net—the net 4*a* of Wells (1956) or the kagomé net of Frank & Kasper (1959)—with Zr atoms symmetrically above and below the hexagonal holes in this plane. These considerations support one's general conception of a metal, that there is no preferred polyhedron around any particular atom, but that any arrangement which satisfies the space group and radius-ratio and gives a reasonably large co-ordination number around each atom is a likely structure.

This work originated in a research programme at the Royal Military College of Science, Shrivenham, under the general direction of Mr C. G. Wilson. The authors would like to thank Mr H. D. Mallon, R.M.C.S., for the preparation and examination of the microstructures of the compound, and also Dr H. W. Ehrlich, Chemistry Department, University of Edinburgh, for helpful discussions. The encouragement of Prof. N. Feather to complete this work is gratefully acknowledged. This paper is published by permission of the Dean of the Royal Military College of Science, Shrivenham.

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Acta Cryst. (1961). **14**, 472

The Separation of Short Range Order and Size Effect Diffuse Scattering

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(*Received* 1 *August* 1960)

Short range order diffuse scattering in binary substitutional solid solutions is often obscured by modulations associated with the fact that the two kinds of atoms are of different sizes. A method is described for the separation of these two components of the diffuse scattering, and it is illustrated by its application to CuAu. It is suggested that a determination of the size effect coefficients along with the short range order parameters will provide a greater insight into the short range structure of an alloy.

Introduction

If the atoms of a binary substitutional solid solution are arranged on the atomic sites such that there is no long range order, superstructure reflections disappear and are replaced by diffuse scattering. The Fourier transform of this short range order diffuse intensity gives the short range order parameters, or the average relative populations of the two kinds of atoms in the various coordination shells about an atom at the origin. Roberts (1954) discovered that the diffuse scattering for the alloy CuAu was modulated in a way not compatible with the cosine Fourier series representation of short range order, and Warren, Averbach & Roberts (1951) showed that these modulations are associated with small static displacements of the atoms from the sites of the average lattice. Such displacements are due, in most metallic solid

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* Operated for the U.S. Atomic Energy Commission by the Union Carbide Corporation.