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The crystal structure of ZrAl.

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The crystal structure of the intermetallic phase ZrAl has been determined from X-ray powder films of impure specimens. Several alloys were prepared by arc melting suitable quantities of the pure metals in argon to give a composition of 50 at.% for each component, but all the films showed the presence of considerable quantities of the neighbouring phase Zr_2Al_3. According to the phase diagram for the zirconium–aluminium system (McPherson & Hansen, 1954), the stable composition range for ZrAl is only a few at.% and furthermore the alloy is unstable above 1250 °C. It is apparent that the preparation of a pure specimen of ZrAl is difficult, and metallographic examination of the polished specimens showed the presence of two phases, Zr_2Al_3 and ZrAl.

The most suitable film for the structure determination was taken by Dr J. Adam of A.E.R.E., Harwell, using a Guinier-type focusing camera with monochromatised Cu $K\alpha$ radiation. The sharply defined lines on this film were carefully examined, and those lines belonging to the Zr_2Al_3 phase, whose structure is now known (Renouf & Beevers, 1961), were rejected. Apart from a few unidentified lines, the remaining lines were indexed on the basis of an orthorhombic unit cell of dimensions similar to that given by Edshammar (1961) for HfAl; the dimensions found were

$$a = 3{\cdot}359 \pm 0{\cdot}001,\quad b = 10{\cdot}887 \pm 0{\cdot}003,\quad c = 4{\cdot}274 \pm 0{\cdot}001\ \text{Å}.$$

The density of the impure bulk specimen was measured using a density bottle and found to be 4·8 g.cm.$^{-3}$; the calculated value of the density, assuming 4 ZrAl per unit cell, is 5·02 g.cm.$^{-3}$. The calculated density of the pure Zr_2Al_3 phase is 4·70 g.cm.$^{-3}$ so that the observed density of 4·8 g.cm.$^{-3}$ corresponds to a mixture of Zr_2Al_3 and ZrAl in the ratio of 2:1 approx. This rough estimate of the specimen composition is in agreement with the observations on the films and the metallographic evidence.

The observed reflections obeyed the following conditions:

$$(hkl)\quad h+k=2n,\ (0kl)\quad k=2n,$$
$$(h0l)\quad l=2n \text{ and } (hk0)\quad h+k=2n,$$

which suggest the space group $Cmcm$–D_{2h}^{17}, which was found by Edshammar for HfAl. The proposed structure was based on that of HfAl and good agreement between observed and calculated intensities (Table 1) is obtained with atoms in the following positions, which were obtained by trial and error:

$$\text{Zr 4 } (c)\ 0, y, \tfrac{1}{4};\quad y = 0{\cdot}16$$
$$\text{Al 4 } (c)\ 0, y, \tfrac{1}{4};\quad y = 0{\cdot}43$$

Further refinement of the atomic parameters is not justified owing to the impure nature of the specimen.

The interatomic distances obtained from this structure are as follows:

4 Zr–Zr	3·35 Å	1 Zr–Al	2·94 Å
2 Zr–Zr	3·36	2 Al–Al	3·36
4 Zr–Al	2·89	2 Al–Al	2·62
2 Zr–Al	3·01		

Table 1

	$\sin^2\theta \times 10^4$		Intensities	
(*hkl*)	Observed	Calculated	Observed	Calculated
(020)	201	201	*w*	22
(021)	523	526	*ms*	91
(110)	577	577	*w*	16
(040)	802	802	*s*	34*
(111)	903	902	*vs*	234
(130)	978	978	*ms*	118
(041)	1128	1127	*m*	96
(002)	1301	1301	*m*	81
(131)		1303		
(150)	1781	1781	*vw*	3*
(060)	1805	1805	*w*	10
(112)	1876	1878	v_2w	6
(042)	2106	2103	*ms*	76
(151)		2106		
(200)		2107		
(061)	2130	2130	*w*	5*
(132)	2278	2279	*ms*	65
(221)	2632	2633	*mw*	21
(240)	2910	2909	v_2w	9
(170)	2983	2984	*w*	17
(152)	3086	3082	*mw*	2*
(023)	3129	3130	v_4w	7
(080)	3209	3209	v_2w	2*
(241)	3229	3234	*m*	36
(171)	3309	3309	*mw*	15*
(202)	3409	3408	*mw*	24
(113)	3504	3505	*mw*	26
(081)	3534	3523	*w*	17
(222)	3612	3609	*vw*	2*
(043)	3730	3730	*w*	14
(260)	3916	3912	*vw*	7
(242)	4217	4206	*mw*	10
(172)	4288	4285	*m*	21*
(153)	4709	4711	*vw*	10
(310)	4793	4790	*vw*	0
(0,10,0)	5015	5014	*w*	4*
(311)	5123	5115	*mw*	16
(004)	5202	5213	*m*	26
(262)		5213		
(330)		5192		
(223)	5241	5238	*w*	8
(024)	5402	5405	*vw*	0*

* Indicates overlapping Zr_2Al_3 lines.

s = strong, *m* = medium, *w* = weak, *v* = very.

The results confirm the isomorphous nature of the intermetallic compounds HfAl and ZrAl. The description of the structure has been given by Edshammar and as stated by that author is in keeping with Frank & Kasper's ideas on the intermetallic structures formed by the transition elements.

The authors wish to thank Mrs J. Thomson, Imperial College, London University, for preparing the specimens, Dr J. Adam, A.E.R.E. Harwell, for help and advice, and Mr H. D. Mallon, R.M.C.S., Shrivenham, for making the metallographic examination.

References

EDSHAMMAR, L. E. (1961). *Acta Chem. Scand.* **15**, 403.
MCPHERSON, D. J. & HANSEN, M. (1954). *Trans. Amer. Soc. Metals*, **46**, 354.
RENOUF, T. J. & BEEVERS, C. A. (1961). *Acta Cryst.* **14**, 469.

Acta Cryst. (1962). **15**, 622

Über die Kristallstruktur des Rhodonits (Mn, Ca) SiO_3. Über die Kristallstruktur des Pyroxmangits (Mn, Fe, Ca, Mg) SiO_3.

Von F. LIEBAU, W. HILMER und G. LINDEMANN. Von F. LIEBAU. *Institut für Anorganische Chemie der Deutschen Akademie der Wissenschaften zu Berlin, Berlin-Adlershof. Deutschland.*

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In den Arbeiten von F. Liebau, W. Hilmer & G. Lindemann (1959*a*) und von F. Liebau (1959*b*) sind infolge von Verschiebungen des Ursprungs während der Untersuchungen Fehler aufgetreten, die wie folgt zu ändern sind:

1.) In den Figuren 3 und 4 beider Arbeiten ist die Richtung der *w*-Achse bzw. der *z*-Achse um 180° zu drehen.
2.) In Tabelle 3 der Rhodonitarbeit sind für die Kationen und die Siliciumatome die angegebenen *z/c*-Werte durch $1-(z/c)$ zu ersetzen, die der Sauerstoffatome durch $1/2-(z/c)$.

Literatur

LIEBAU, F., HILMER, W. & LINDEMANN, G. (1959*a*). *Acta Cryst.* **12**, 182.
LIEBAU, F. (1959*b*). *Acta Cryst.* **12**, 177.

Acta Cryst. (1962). **15**, 622

Unit cell and space group of L-proline monohydrate. A correction.

By V. SASISEKHARAN, *Department of Physics, University of Madras, Madras 25, India.*

In the paper by Sasisekharan (1959) the *h*0*l* systematic absences are incorrectly reported; they should be

*h*0*l* reflections—only *h* even present.

The space-group deduction is unchanged.

H. LIPSON

Reference

SASISEKHARAN, V. (1959). *Acta Cryst.* **12**, 941.

Book Reviews

Works intended for notice in this column should be sent direct to the Editor (A. J. C. Wilson, Department of Physics, University College, Cathays Park, Cardiff, Great Britain). As far as practicable books will be reviewed in a country different from that of publication.

Organic Chemical Crystallography.

By A. I. KITAIGORODSKII [Kitajgorodskij]. Pp. x+541. New York: Consultants Bureau. 1961. Price $17·50.

This book is the translation of a Russian text published in 1955 (with a few sections added). The first chapter is a consideration of molecular sizes and shapes, based on Sutton's book 'Interatomic Distances', and on intermolecular distances from X-ray crystallographic results. By comparisons of related molecules some rough computations of deformation forces are made. Then follow some calculations of the volume increments when certain common groups are added to a number of molecules. The chapter concludes with a well-written account of molecular symmetry.

Chapter 2 gives a clear account of lattice and space-group theory. It is interesting here to see that credit is given only to Fedorov for the elucidation of the space group, and that the modern symbolism is described as the 'International' rather than the Hermann–Mauguin system. The Schoenfliess system is also given, but not by name, and it is appropriately described as 'illogical'.

Chapter 3 is a detailed study of the symmetry of objects in chains, layers and in three-dimensional lattices. The author uses his own notation, and the discussion is made difficult to follow by the introduction of special terms, such as 'unit', 'strip', 'axis of gravity' all of which are not very clearly defined. However the general conclusion is plain enough, it is that some space groups permit close-packing much more readily than others. The author then compares his results with the statistical findings of Nowacki, and does not hesitate to sweep away some of the early space-group determinations when they disagree with his theories. In this chapter also is a table of 'packing coefficients' in aromatic compounds, i.e. the ratio of inherent molecular volume to the total cell volume. The author attaches considerable significance to this quantity.