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The Crystal Structure of Hexagonal Rh_2Al_5

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The crystal structure of hexagonal Rh_2Al_5 has been determined and refined by least squares techniques on the basis of three-dimensional X-ray data. The structure is of the Co_2Al_5-type. The dimensions of the unit cell are $a = 7.893$ Å and $c = 7.854$ Å. The interatomic distances of Rh_2Al_5 are compared to those of Co_2Al_5. Phase-analytic observations in the region $RhAl_{1.0}$-$RhAl_{2.5}$ are given.

No systematic investigation of the rhodium-aluminium system seems to have been reported in literature. However, the structure of RhAl has been given by Schubert *et al.* as being of the CsCl-type.[1] This paper concerns phase relationships in the compositional region $RhAl_{1.0-2.5}$ and the crystal structure of a phase Rh_2Al_5 formed at 850°C.

EXPERIMENTAL

The alloys were prepared from rhodium powder (L. Light & Co., about 99.98 %) and aluminium ribbon (E. Merck A. G., at least 99.99 %) by arc-melting in an argon atmosphere with the sample resting on a water-cooled copper base. The alloys thus obtained were then lump-annealed for one week at 850°C in sealed, evacuated silica tubes. The heat-treatment was discontinued by quenching the tubes in water.

Powder patterns were obtained in a Guinier camera with Cu$K\alpha_1$ radiation and with KCl as an internal standard. Single crystal data were collected in a Weissenberg camera using CuK radiation and the intensities were estimated visually.

The computational work was carried out on FACIT EDB with programs numbered 6018 (L-p correction) and 6023 (least squares) in the *World List of Crystallographic Computer programs*.[2]

PHASE ANALYSIS

Arcmelted samples in the composition range $RhAl_{1.0-2.5}$ gave powder patterns that showed the existence of one phase at RhAl and a second phase close to the composition $RhAl_{2.5}$. RhAl was found to be of the CsCl-type with the cell constant $a = 2.97$ Å, *i.e.* somewhat smaller than the earlier reported 2.99 Å.[1] However, the pattern of RhAl is rather diffuse at the equi-atomic composition. The sharp patterns of this phase present in photographs of

$RhAl_{1.2}$, $RhAl_{1.5}$, and $RhAl_{1.75}$ gave identical cubic constants $a = 2.970 \pm 0.002$ Å.

The patterns of arcmelted samples around $RhAl_{\sim 2.5}$ could be indexed by assuming a cubic cell. The positions of the powder lines change with the composition and the cubic constant is $a = 15.35$ Å in the region $RhAl_{1.5-<2.5}$ but $a = 15.32$ Å at compositions very close to $RhAl_{2.5}$. Further studies on this compositional region are in progress by single crystal methods.

In specimens $RhAl_{1.0-2.5}$ heat-treated at 850°C two phases were observed *viz.* the CsCl-type phase with $a = 2.970 \pm 0.002$ Å (*v. supra*) and a hexagonal phase with $a = 7.893$ Å and $c = 7.854$ Å at the composition $RhAl_{2.50}$. No change in these parameters was observed when comparing the powder photographs recorded in the region $RhAl_{2.0-3.0}$.

THE STRUCTURE OF Rh_2Al_5

The structure of the hexagonal phase $RhAl_{2.5}$ mentioned above was then investigated. The appearance of the powder pattern, the composition and the unit cell dimensions suggested the structure to be isomorphous with Co_2Al_5. A small irregular crystal (less than 0.02 mm in all dimensions) found in a crushed sample of the stoichiometric composition was used in the single crystal work. Weissenberg photographs of five layer lines were registered along an *a*-axis. The reflections were indexed in terms of the orthohexagonal cell and 230 independent intensities were estimated.

The atomic parameters given by Bradley and Cheng [3] for Co_2Al_5 were adopted as a starting point for the refinement which was performed by means of the least-squares technique. The computer program does not permit higher symmetry than orthorhombic to be treated and for that reason the structure of Rh_2Al_5 had to be described using the orthohexagonal cell. The final *R*-value was 0.118. The structure thus obtained is the following.

Space group: $P6_3/mmc$ (No. 194)

Unit-cell contents: 4 Rh_2Al_5

Al_1	in	2(*a*):	0,0,0		$B = 0.9 \pm 0.4$ Å^2
Al_2	in	6(*h*):	*x*,2*x*,1/4	$x = 0.473 \pm 0.002$	$B = 1.0 \pm 0.4$
Al_3	in	12(*k*):	*x*,2*x*,*z*	$x = 0.193 \pm 0.002$ $z = -0.058 \pm 0.002$	$B = 1.1 \pm 0.4$
Rh_1	in	2(*d*):	2/3,1/3,1/4		$B = 0.48 \pm 0.06$
Rh_2	in	6(*h*):	*x*,2*x*,1/4	$x = 0.1308 \pm 0.0006$	$B = 0.48 \pm 0.06$

Table 1 gives the powder data of Rh_2Al_5 and a comparison between observed and calculated intensities.

DISCUSSION

The structure of Co_2Al_5 was first reported by Bradley and Cheng [3] who also gave a careful description of the atomic arrangement of this compound. The structure was later confirmed and refined by Newkirk, Black and Damjanovic.[4] The structure of Rh_2Al_5 deviates very little from that of Co_2Al_5.

Table 1. The Guinier powder pattern of Rh_2Al_5 ($CuK\alpha_1$).

h k l	$\sin^2\theta_{obs}$	$\sin^2\theta_{calc}$	I_{obs}	I_{calc}
1 0 0	0.01272	0.01270	m	> 10
1 0 1	0.02234	0.02231	w	5.5
1 1 0		0.03809	—	0.1
0 0 2	0.03852	0.03846	st	308.1
2 0 0	0.05083	0.05079	m	118.0
1 0 2	0.05120	0.05116	vvw	9.3
2 0 1	0.06041	0.06041	vst	607.0
1 1 2	0.07670	0.07656	vvw	5.2
2 1 0	0.0892	0.08889	diff w	17.4
2 0 2		0.08926		22.8
2 1 1	0.09842	0.09850	vvw	3.2
1 0 3	0.09939	0.09924	vvw	4.8
3 0 0	0.11431	0.11428	w	19.1
3 0 1	0.12392	0.12390	st	296.7
2 1 2	0.12728	0.12735	vst	365.2
2 0 3	0.13733	0.13734	vst	462.5
2 2 0	0.15230	0.15238	m+	225.0
3 0 2		0.15275	—	4.9
0 0 4	0.15379	0.15386	m	109.6
3 1 0		0.16507	—	1.3
1 0 4	0.16655	0.16655	w	13.3
3 1 1	0.17460	0.17469	m	90.1
2 1 3		0.17543	—	3.9
2 2 2	0.19090	0.19084	m—	64.8
1 1 4		0.19195	vvw	3.7
3 0 3	0.20079	0.20083	m—	60.3
4 0 0	0.20330	0.20317	vw	11.3
3 1 2		0.20354	—	5.9
2 0 4	0.20477	0.20465	vw	10.3
4 0 1	0.21275	0.21278	w	23.3
2 3 0	0.2413	0.24126	diff w	23.9
4 0 2		0.24163		14.7
2 1 4	0.24272	0.24274	w	42.0

The rhodium radius is about 0.1 Å larger than the cobalt radius (r_{Rh} = 1.35 Å and r_{Co} = 1.25 Å) and this difference is clearly reflected in the interatomic distances in Rh_2Al_5 and Co_2Al_5 (*cf.* Table 2) as well as in RhAl and CoAl which are both of the CsCl-type with Rh—Al = 2.58 Å and Co—Al = 2.48 Å. According to Table 2 there are three kinds of Rh—Al distances all approximately 0.1 Å longer than the equivalent ones in Co_2Al_5, *viz.* Rh_1—Al_3, Rh_2—Al_1 and the second Rh_2—Al_3. However, the remaining Rh—Al distances Rh_1—Al_2, Rh_2—Al_2 and the first Rh_1—Al_3 are only about 0.05 Å longer than the corresponding distance in the cobalt phase.

The interaluminium distances are all longer than the equivalent ones in Co_2Al_5. This is obviously caused by expansion due to the size of the rhodium atoms. However, the expansion of the aluminium skeleton seems to be larger than necessary for this reason as illustrated by the mean atomic volumes in Fig. 1. (Mean atomic volume = cell volume divided by the number of atoms in the unit cell.) Rh_2Al_5 shows a positiv deviation from a line drawn between

Table 2. Interatomic distances in Rh_2Al_5 compared to distances in Co_2Al_5.

Atom	Neighbour	Number of neighbours	Interatomic distances in Rh_2Al_5	Equivalent distances in Co_2Al_5	Difference in distances
Al_1—	Rh_2	6	2.66 Å	2.54 Å	0.12 Å
	Al_3	6	2.68	2.62	0.06
Al_2—	Rh_1	1	2.65	2.61	0.04
	Rh_2	2	2.46	2.41	0.05
	Al_2	2	3.31	3.14	0.17
	Al_3	4	2.81	2.74	0.07
	Al_3	4	3.07	2.97	0.10
Al_3—	Rh_1	1	2.44	2.35	0.09
	Rh_2	2	2.78	2.70	0.08
	Rh_2	1	2.56	2.51	0.05
	Al_1	1	2.68	2.62	0.06
	Al_2	2	2.81	2.74	0.07
	Al_2	2	3.07	2.96	0.11
	Al_3	1	3.02	2.92	0.10
	Al_3	2	2.79	2.73	0.06
	Al_3	2	3.32	3.19	0.13
Rh_1—	Al_2	3	2.65	2.61	0.04
	Al_3	6	2.44	2.35	0.09
Rh_2—	Rh_2	2	3.10	2.91	0.19
	Al_1	2	2.66	2.54	0.12
	Al_2	2	2.46	2.41	0.05
	Al_3	2	2.56	2.51	0.05
	Al_3	4	2.78	2.70	0.08

RhAl and Al whereas Co_2Al_5 is situated on the CoAl—Al line. This difference is likely to indicate that the structural details of these phases are influenced not only by atomic size but that the electronic structure may also effect the cell volume.

Further studies on this system are in progress. The cubic high-temperature phase mentioned in the phase analysis is being investigated together with a similar phase found in the iridium-aluminium system.

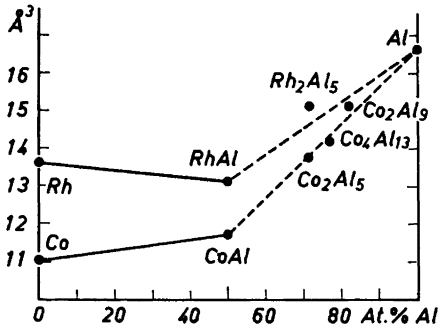

Fig. 1. Mean atomic volumes of cobalt-aluminium and rhodium-aluminium compounds.

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