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The Crystal Structure of Rh_2Al_9 and Ir_2Al_9

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The phases Rh_2Al_9 and Ir_2Al_9 have been synthesized and found to be isomorphous with Co_2Al_9. The unit cell dimensions are

Rh_2Al_9: $a = 6.352$, $b = 6.428$, $c = 8.721$ Å and $\beta = 94.81°$
Ir_2Al_9: $a = 6.378$, $b = 6.430$, $c = 8.732$ Å and $\beta = 94.77°$

The crystal structure of Rh_2Al_9 has been refined with least squares techniques to an R value of 0.09 using three-dimensional Weissenberg data. The interatomic distances are compared to those in Co_2Al_9.

The existence of the phase Rh_2Al_9 was first established by Ferro *et al.* in their phase analysis investigation of the rhodium-aluminium system.[1] However, no crystallographic data were given for this compound. No similar investigation seems to have been reported on the iridium-aluminium system. An X-ray investigation on Rh_2Al_9 and Ir_2Al_9, which will be described in the present paper, shows that the compounds are isostructural and of the Co_2Al_9 type.

EXPERIMENTAL

An alloy of the composition $RhAl_{4.5}$ was prepared from rhodium powder (L. Light & Co., about 99.98 %) and aluminium ribbon (E. Merck AG., at least 99.99 %) by arc-melting in an argon atmosphere with the sample resting on a water-cooled copper base. The alloy was then lump-annealed for four days at 660°C in a sealed evacuated silica tube. The heat-treatment was discontinued by quenching in water. The alloy thus obtained was crystalline and good single crystals suitable for a Weissenberg recording were easily found. No chemical analysis was performed as the weight loss during the preparation was very small.

The compound Ir_2Al_9 was prepared in an analogous way. The iridium powder used has a purity of 99.98 % according to the supplier (L. Light & Co., about 99.98 %). No useful single crystals could be found in the quenched product.

Powder patterns were obtained in a Guinier-Hägg camera with Cu$K\alpha_1$ radiation ($\lambda = 1.54050$ Å) and with KCl ($a = 6.2919$ Å) as an internal standard.

Single crystal data of Rh_2Al_9 were collected with a Nonius Weissenberg camera using CuK radiation. The multiple film technique was used and the intensities were estimated visually by comparison with an intensity scale prepared from a suitable reflection of the zero layer.

The computational work was carried out on the CD 3600 computer at Uppsala. Lp correction was performed with a program called DRF (by A. Zalkin, modified by

R. Liminga and J.-O. Lundgren, Uppsala) and least squares refinements of positional parameters and temperature factors were performed with LALS (by A. Zalkin, modified by R. Liminga, J.-O. Lundgren and C.-I. Brändén).

THE PHASE Rh_2Al_9

A small irregular crystal (all dimensions less than 0.02 mm) found in the quenched sample of the composition $RhAl_{4.5}$ was used in the single crystal work. The Weissenberg data obtained showed clearly that they were generated by a structure isomorphous with the earlier known Co_2Al_9.[2] Approximate cell dimensions were determined from these data. The powder pattern of the sample was indexed and after a least squares refinement the following unit cell dimensions were obtained:

$$a = 6.352 \pm 0.001 \text{ Å}, \; b = 6.428 \pm 0.001 \text{ Å}, \; c = 8.721 \pm 0.001 \text{ Å},$$
$$\beta = 94.81° \pm 0.02°$$

The powder pattern of Rh_2Al_9 is given in Table 1. No change of this pattern was observed for alloys of different compositions around $RhAl_{4.5}$.

Table 1. The powder pattern of Rh_2Al_9 ($CuK\alpha_1$, $\lambda = 1.5405$ Å).

$h\,k\,l$	$\sin^2\theta_{obs}$	$\sin^2\theta_{calc}$	I_{obs}	I_{calc}
1 0 0	—	0.01481	—	0.2
0 1 1	0.02225	0.02222	m	40.0
1 1 0	0.02919	0.02917	st	96.6
0 0 2	0.03147	0.03142	w	23.1
$\bar{1}$ 1 1	0.03515	0.03522	m	76.3
1 1 1	0.03886	0.03883	m	74.7
$\bar{1}$ 0 2	0.04264	0.04262	m	50.0
0 1 2	0.04576	0.04578	m	62.1
1 0 2	0.04987	0.04985	m	45.0
$\bar{1}$ 1 2	0.05699	0.05697	vw	9.3
0 2 0	—	0.05744	—	0.1
2 0 0	0.05927	0.05923	m	46.1
1 1 2	0.06431	0.06421	vw	7.9
0 2 1	0.06529	0.06529	m	59.4
1 2 0	—	0.07225	—	1.1
2 1 0	—	0.07359	—	0.4
$\bar{2}$ 1 1	0.07790	0.07783	vw	5.8
$\bar{1}$ 2 1	—	0.07829	—	0.1
1 2 1	0.08190	0.08191	vw	4.1
$\bar{2}$ 0 2	0.08335	0.08342	w	14.7
2 1 1	0.08509	0.08506	w	2.7
0 1 3		0.08506		19.6
0 2 2	—	0.08886	—	0.3
$\bar{1}$ 1 3	0.09443	0.09444	—	2.2
$\bar{2}$ 1 2	—	0.09777	—	1.4
2 0 2	—	0.09789	—	0.5
$\bar{1}$ 2 2	0.09999	0.10005	w	23.4
1 1 3	0.10531	0.10530	vw	3.9
1 2 2	0.10731	0.10729	w	32.1
2 1 2	0.11221	0.11225	m	59.2
$\bar{2}$ 2 0	—	0.11667	—	0.0
$\bar{2}$ 2 1	0.12092	0.12090	m	44.5
0 0 4	0.12574	0.12569	vw	6.8

Table 2. Final atomic parameters of Rh_2Al_9. Space group: $P2_1/c$; $Z=2$.

	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B Å^2	$\sigma(B)$
Rh in 4*e*	0.2630	0.0003	0.62194	0.0005	0.3313	0.0002	0.77	0.06
Al_0 in 2*a*	—	—	—	—	—	—	1.80	0.21
Al_1 in 4*e*	0.4031	0.0011	0.9790	0.0020	0.2678	0.0008	1.32	0.14
Al_2 in 4*e*	0.0951	0.0011	0.2874	0.0019	0.2277	0.0008	1.21	0.14
Al_3 in 4*e*	0.3895	0.0011	0.1956	0.0019	0.9982	0.0008	1.15	0.14
Al_4 in 4*e*	0.2161	0.0012	0.6099	0.0019	0.0415	0.0008	1.38	0.14

The atomic parameters given by Douglas [2] for Co_2Al_9 were adopted as starting values in the least squares refinement. This was based on 380 measured reflections, all of them independent, collected with the crystal rotating around the monoclinic axis. The weights were calculated using Hughes' weighting scheme. Atomic scattering factors including the real part of the dispersion correction were taken from the *International Tables for X-Ray Crystallography*.

Table 3. Interatomic distances in Rh_2Al_9 and their e.s.d.'s in Å.

Rh—Al_0	2.446	0.002	Al_3—Rh	2.595	0.012
Al_4	2.521	0.009	Rh	2.599	0.008
Al_2	2.525	0.008	Al_1	2.728	0.014
Al_1	2.529	0.008	Al_0	2.776	0.008
Al_2	2.533	0.012	Al_4	2.847	0.011
Al_1	2.539	0.012	Al_3	2.879	0.023
Al_4	2.551	0.011	Al_2	2.886	0.011
Al_3	2.595	0.012	Al_1	2.906	0.016
Al_3	2.599	0.008	Al_2	2.912	0.011
			Al_4	2.918	0.017
Al_0—2Rh	2.446	0.002	Al_1	2.961	0.014
2Al_2	2.742	0.011	Al_1	2.982	0.013
2Al_3	2.776	0.008			
2Al_2	2.848	0.010	Al_4—Rh	2.521	0.009
2Al_4	2.867	0.012	Rh	2.551	0.011
			Al_2	2.781	0.016
Al_1—Rh	2.529	0.008	Al_1	2.812	0.012
Rh	2.539	0.012	Al_3	2.847	0.011
Al_3	2.728	0.014	Al_0	2.867	0.012
Al_2	2.786	0.014	Al_3	2.918	0.017
Al_4	2.812	0.012	Al_1	2.941	0.011
Al_3	2.906	0.016	Al_2	3.013	0.011
Al_4	2.941	0.011	Al_4	3.118	0.016
Al_3	2.961	0.014	Al_2	3.151	0.012
Al_3	2.982	0.013	Al_1	3.247	0.015
Al_4	3.247	0.015			
Al_2—Rh	2.525	0.008			
Rh	2.533	0.012			
Al_0	2.742	0.011			
Al_4	2.781	0.016			
Al_1	2.786	0.014			
Al_0	2.848	0.010			
Al_3	2.886	0.011			
Al_3	2.912	0.011			
Al_4	3.013	0.011			
Al_4	3.151	0.012			

The following 25 parameters were refined: four scale factors corresponding to each one of the collected layer-lines, 15 positional parameters and 5 isotropic temperature factors. After six cycles of full-matrix refinement, an R value of 0.10 was obtained for the 380 reflections. 19 of the reflections were rejected by the program and if these were not included the R-value was 0.09. The final structural data of Rh_2Al_9 are given in Table 2 and the interatomic distances are given in Table 3.

THE PHASE Ir_2Al_9

A comparison between the powder films taken from Ir_2Al_9 and Rh_2Al_9 showed the structures to be isomorphous. The cell dimensions of Ir_2Al_9 were refined by the least squares method and the following constants were found:

$$a = 6.378 \pm 0.001 \text{ Å}, \; b = 6.430 \pm 0.001 \text{ Å}, \; c = 8.732 \pm 0.002 \text{ Å},$$
$$\beta = 94.77° \pm 0.02°$$

The powder pattern of Ir_2Al_9 is given in Table 4. No changes of the unit cell dimensions were observed for alloys of different compositions around $IrAl_{4.5}$.

Table 4. The powder pattern of Ir_2Al_9 ($CuK\alpha_1$, $\lambda = 1.5405$ Å).

$h\ k\ l$	$\sin^2\theta_{obs}$	$\sin^2\theta_{calc}$	I_{obs}
1 0 0	0.01472	0.01469	vvw
0 1 1	0.02214	0.02218	m
1 1 0	0.02906	0.02904	vst
0 0 2	0.03138	0.03134	m
$\bar{1}$ 1 1	0.03503	0.03509	st
1 1 1	0.03866	0.03866	st
$\bar{1}$ 0 2	0.04244	0.04246	st
0 1 2	0.04570	0.04569	st
1 0 2	0.04960	0.04960	st
$\bar{1}$ 1 2	0.05687	0.05681	w
0 2 0	—	0.05740	—
2 0 0	0.05874	0.05874	st
1 1 6	0.06406	0.06394	vw
0 2 1	0.06529	0.06523	st
1 2 0	—	0.07209	—
2 1 0	—	0.07309	—
$\bar{2}$ 1 1	0.07736	0.07736	vw
$\bar{1}$ 2 1	0.07813	0.07814	vvw
1 2 1	0.08173	0.08171	w
$\bar{2}$ 0 2	0.08301	0.08295	w
2 1 1	—	0.08449	—
0 1 3	0.08492	0.08487	m
0 2 2	—	0.08874	—
$\bar{1}$ 1 3	—	0.09420	—
2 0 2	—	0.09722	—
$\bar{2}$ 1 2	0.09741	0.09730	vvw
$\bar{1}$ 2 2	0.09980	0.09986	w
1 1 3	—	0.10490	—
1 2 2	0.10697	0.10700	w
2 1 2	0.11161	0.11157	m+
$\bar{2}$ 2 0	—	0.11614	—
$\bar{2}$ 2 1	0.12035	0.12041	m+
0 0 4	—	0.12536	—

DISCUSSION

The structure of Co_2Al_9 has been described by Schubert [3] as a stacking of alternating quadratic layers of Al and $CuAl_2$.

The structure of Rh_2Al_9 is strictly isomorphous with Co_2Al_9. The differences found between the two structures depend on the fact that the rhodium radius is about 0.1 Å larger than the cobalt radius. Thus, the Rh—Al distances in Rh_2Al_9 range from 2.45 Å to 2.60 Å and have an average value of 2.54 Å, whilst the Co—Al distances in Co_2Al_9 lie within the range 2.37—2.50 Å, with an average of 2.47 Å. This comparison is in concordance with a similar one made for the Rh—Al and Co—Al bonds in the two isostructural compounds Rh_2Al_5 and Co_2Al_5.[4]

The interaluminium distances in Rh_2Al_9 range from values that are the same up to values 0.12 Å larger than those of the equivalent distances in Co_2Al_9. This is also in agreement with comparisons between Rh_2Al_5 and Co_2Al_5.

Further studies on the Rh—Al and the Ir—Al systems are in progress.

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