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The Crystal Structure of Pt_8Al_{21}

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The crystal structure of Pt_8Al_{21} has been determined on the basis of three-dimensional X-ray single crystal data. The symmetry is tetragonal, space group No. 88, $I4_1/a$, and the unit cell contains four formula units. The cell dimensions are:

$$a = 12.97 \text{ Å}, \quad c = 10.65 \text{ Å}.$$

The interatomic distances and the mean atomic volume are discussed and compared with those of $PtAl_2$ (CaF_2-type).

The platinum-aluminium phase diagram has been described by Huch and Klemm,[1] who found the following phases: $PtAl_4$, $PtAl_3$, $PtAl_2$, Pt_2Al_3, PtAl, Pt_3Al_2, Pt_5Al_3, Pt_3Al, and $Pt_{13}Al_3$. The crystal structures were given for $PtAl_2$ (CaF_2), Pt_2Al_3 (Ni_2Al_3-like), PtAl (FeSi), Pt_5Al_3 (Rh_5Ge_3), and Pt_3Al (Cu_3Au).

The present work establishes the existence of a Pt_8Al_{21} phase. The structure of this phase has been determined and it is suggested that it corresponds to the $PtAl_3$ phase described by Huch and Klemm. The Debye-Scherrer photograph of the preparation of composition $PtAl_3$ given by these authors is in agreement with the powder pattern yielded by Pt_8Al_{21} in this investigation.

EXPERIMENTAL

Weighed amounts of platinum (Baker platinum, about 99.9 % pure) and aluminium (E. Merck A. G. at least 99.99 % pure) were melted together in an arc-furnace under an argon pressure of about 0.5 atm. The behaviour of the arc-melts at compositions around $PtAl_{2.6}$, and at higher aluminium contents is remarkable. The melts swell, when solidifying, to form porous crystalline masses, several times more voluminous than the melts. An irregular single crystal smaller than 0.01 mm in all dimensions was found in such a product of the composition $PtAl_{2.6}$ and it was used in the single crystal work.

The powder pattern of $PtAl_{2.6}$ could be indexed by assuming a tetragonal cell. The cell dimensions were calculated from a photograph taken with a Guinier type focusing camera using Cu$K\alpha_1$ radiation. Potassium chloride was used as an internal standard. The cell dimensions found are: $a = 12.97 \pm 0.01$ Å, $c = 10.65 \pm 0.01$ Å.

Weissenberg photographs were taken with rotation around the a- and c-axes. The reflections were recorded with the multiple film technique using CuK radiation and the relative intensities were estimated visually by comparison to an intensity scale obtained

Table 1. The structure of Pt_8Al_{21}. Space group: No. 88, $I4_1/a$ (origin at $\bar{4}$). Unit cell dimensions: $a = 12.97$ Å, $c = 10.65$ Å. Cell content: 4 Pt_8Al_{21}.

Atom	Position	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B Å^2	$\sigma(B$ Å$^2)$
Pt_1	16 *f*	0.0926	0.0002	0.1299	0.0002	0.1554	0.0003	0.44	0.05
Pt_2	16 *f*	0.0985	0.0002	0.2851	0.0002	0.7907	0.0003	0.41	0.05
Al_3	16 *f*	0.071	0.002	0.091	0.002	0.771	0.003	0.9	0.4
Al_4	16 *f*	0.082	0.002	0.254	0.002	0.548	0.003	0.1	0.4
Al_5	16 *f*	0.053	0.002	0.089	0.002	0.400	0.003	0.6	0.4
Al_6	16 *f*	0.210	0.002	0.218	0.002	0.978	0.003	0.3	0.4
Al_7	16 *f*	0.223	0.002	0.008	0.002	0.022	0.003	0.4	0.4
Al_8	4 *a*	0		0		0		0.2	0.4

from a reflection from the same crystal. 450 independent intensities ($hk0-hk5$) were collected.

The computational work in this study, including Lorentz-polarization correction (No. 6018), least squares refinement (No. 6023), Fourier summations (No. 6014), calculation of structure factors (No. 6015), and interatomic distances (No. 6016) was performed on the electronic computers FACIT EDB and BESK. The program numbers refer to the *World List of Crystallographic Computer Programs*.[2]

DERIVATION OF THE STRUCTURE

The Weissenberg photographs confirmed the tetragonal symmetry. Reflections hkl were observed only for $h+k+l = 2n$, $hk0$ for h and $k = 2n$ and $00l$ for $l = 4n$. The intensities of the hkl reflections were different from those of the khl reflections. These criteria are characteristic of the space group $I4_1/a$.

From considerations of the composition, the cell volume and the appearance of the Patterson projection along [001] it was found likely that the platinum atoms are situated in two 16*f* positions of $I4_1/a$. The x and y coordinates of these atoms were found in the Patterson projection and they were refined by means of electron density projections. Some minor peaks likely to be due to aluminium atoms were also found in these projections and these (Al_5, Al_7, and Al_8, *cf.* Table 1 and Fig. 2) were included in the calculations. The sites of the Al_3 and Al_5 atoms could then be deduced while Al_4 was not found because of overlapping in the projection.

A three-dimensional analysis was then started. The z coordinates of Pt_1 and Pt_2 were found in the Patterson projection along [010] by assuming that the distances between the platinum atoms should be about the same in this structure as in the earlier known structure of $PtAl_2$. A three-dimensional model was built on the basis of the platinum metal positions thus obtained. All the aluminium sites were then derived by means of the information described above and by packing considerations.

A difference Fourier along [001] showed the tentative structure to be essentially correct and therefore a least squares refinement was started. The computer program applied does not allow a higher symmetry than orthorhombic to be treated in the refining process. Therefore, the 16*f* position of $I4_1/a$ (origin at $\bar{1}$) had to be broken down into two eightfold positions. The calculations involved 42 atomic parameters, 6 scale factors, and 15 isotropic temperature factors. This yields a total of 63 parameters and a ratio of about 7 observed structure factors per parameter to be determined.

After seven cycles of refinement the residual, R, remained stationary at the value 0.123. The errors of the strongest observed reflections turned out to be very high and therefore twenty of these were excluded in a second round of calculations, when an R-value of 0.095 was obtained. The positional parameters were the same in the two calculations but the temperature factors were higher in the second one.

The final results including the atomic parameters and their estimated standard deviations are given in Table 1. The temperature factors are those obtained in the second calculation.

A final check on the structure was then made using all the 57 observed $hk0$ reflections. These gave an R-value of 0.108 with the calculated structure factors. No temperature factor correction was applied here since the overall

factor proved to be about zero when the strongest observed reflections were included in the calculation. The difference Fourier projections calculated from these structure factors are shown in Figs. 1a and 1b.

Table 2. The interatomic distances in Pt_8Al_{21}. Upper limit 3.2 Å. The numbers represent: central atom, neighbour (number of such neighbours), followed by the distance in Å.

1—3(1)	2.62	3—1(1)	2.72	5—1(1)	2.69	7—1(1)	2.71
3(1)	2.72	1(1)	2.62	2(1)	2.63	1(1)	2.60
4(1)	2.59	2(1)	2.55	2(1)	2.59	1(1)	2.52
5(1)	2.69	2(1)	3.08	3(1)	2.61	2(1)	2.56
6(1)	2.67	3(1)	2.99	3(1)	2.81	3(1)	2.98
6(1)	2.76	4(1)	3.17	4(1)	2.67	3(1)	3.01
7(1)	2.71	4(1)	2.93	4(1)	2.74	4(1)	3.10
7(1)	2.60	5(1)	2.81	5(1)	2.71	5(1)	2.84
7(1)	2.52	5(1)	2.61	5(1)	2.88	6(1)	2.76
8(1)	2.65	6(1)	3.17	5(1)	2.88	6(1)	2.83
		7(1)	2.98	7(1)	2.84	8(1)	2.90
2—3(1)	2.55	7(1)	3.01				
3(1)	3.08	8(1)	2.86	6—1(1)	2.67	8—1(4)	2.65
4(1)	2.63			1(1)	2.76	3(4)	2.86
4(1)	2.57	4—1(1)	2.59	2(1)	2.61	7(4)	2.90
4(1)	2.64	2(1)	2.63	2(1)	2.66		
5(1)	2.63	2(1)	2.57	3(1)	3.17		
5(1)	2.59	2(1)	2.64	4(1)	2.83		
6(1)	2.61	3(1)	3.17	6(1)	2.83		
6(1)	2.66	3(1)	2.93	6(1)	2.83		
7(1)	2.56	4(1)	2.69	7(1)	2.76		
		5(1)	2.67	7(1)	2.83		
		5(1)	2.74				
		6(1)	2.83				
		7(1)	3.10				

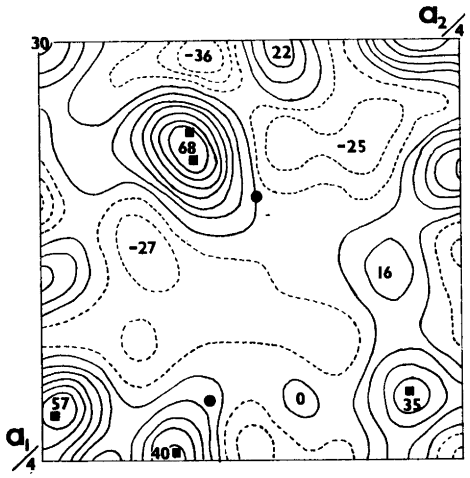

Fig. 1a. The difference synthesis $\varrho(F(hk0)_{obs}-F(hk0)_{Pt})$. ■ positions of aluminium atoms. ● positions of platinum atoms.

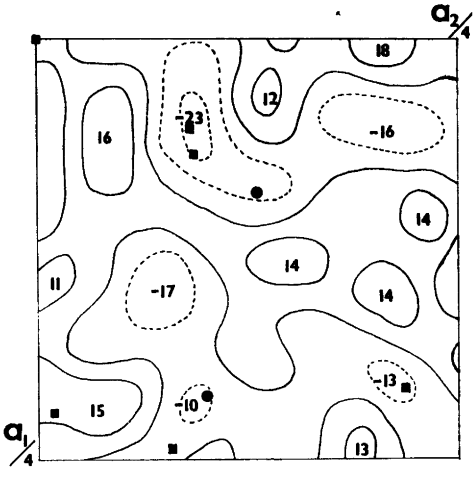

Fig. 1b. The difference synthesis $\varrho(Fhk0)_{obs}-F(hk0)_{calc.})$

DISCUSSION

The complicated and rather irregular crystal structure of Pt_8Al_{21} thus derived is illustrated in Fig. 2 and the interatomic distances are given in Table 2. The standard deviations are less than 0.07 Å for the aluminium-aluminium distances and 0.05 Å for the platinum-aluminium distances.

The surroundings of the two kinds of platinum atoms are indicated in Fig. 2. The arrangement of the upper coordination figure, around Pt_1, is similar to the surrounding of platinum in $PtAl_2$. This phase is of the CaF_2 structure type with platinum situated at the center of a cube formed by eight aluminium atoms at a distance of 2.56 Å from the Pt atom. In Pt_8Al_{21} a distorted Al cube can be identified around Pt_1, which, however, has ten aluminium neighbours at an average distance of 2.65 Å.

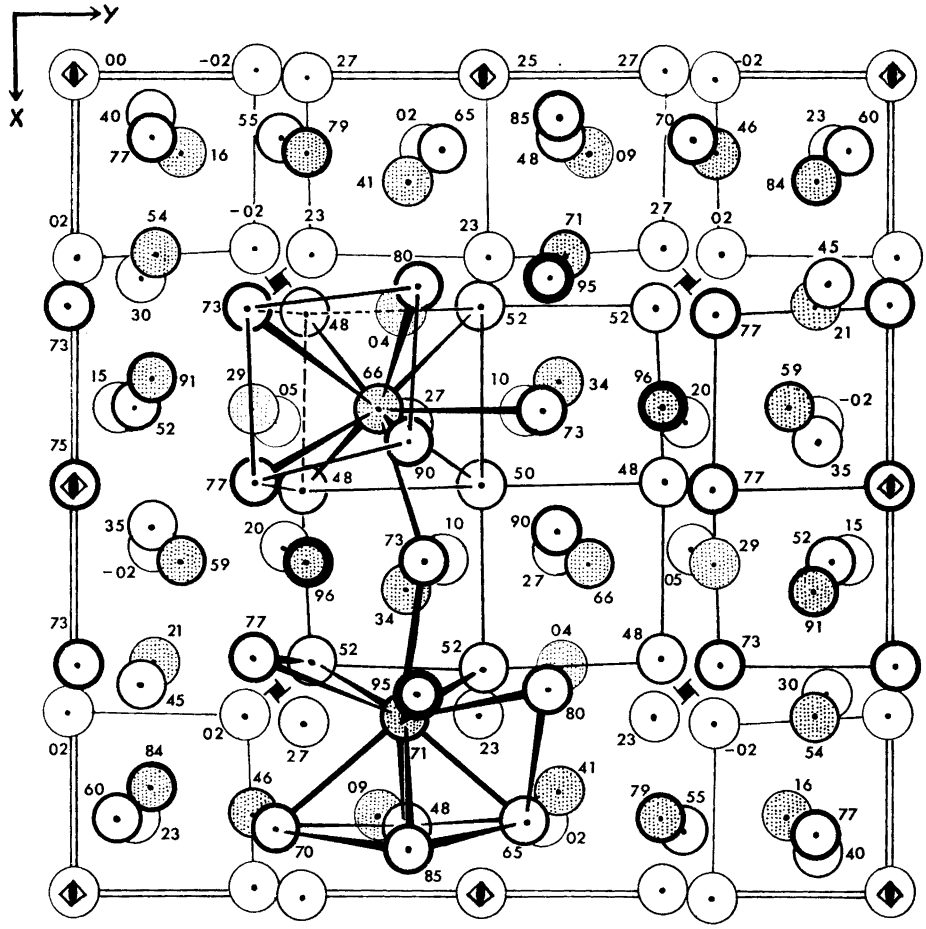

Fig. 2. The crystal structure of Pt_8Al_{21} viewed along [001]. The platinum atoms are dotted. The figures indicate the height, z, in percent of c.

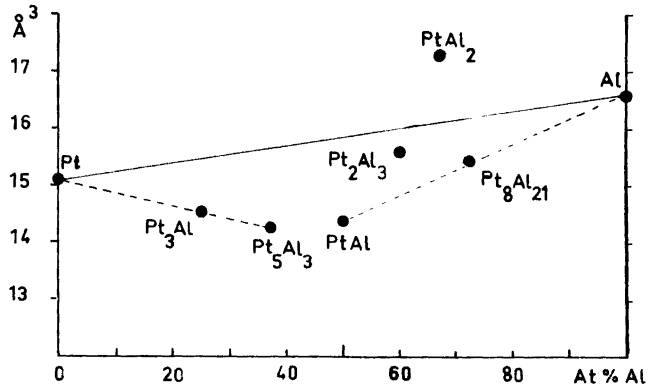

Fig. 3. The mean atomic volume of platinum-aluminium compounds.

The arrangement of aluminium around Pt_2 is very different. This atom has nine aluminium neighbours at an average distance of 2.60 Å which is about the mean value of the two distances given above for eight and tenfold coordination.

The aluminium atom of $PtAl_2$ is 4+6 coordinated with platinum and aluminium atoms, respectively, at the distances 2.56 Å and 2.96 Å. The aluminium atoms of Pt_8Al_{21} have coordinations of ten or higher. The shortest aluminium-aluminium distance is 2.61 Å, *i.e.* about the same as the shortest one found in Pt_2Al_3, *viz.* 2.57 Å.[1] The distribution of the aluminium-aluminium distances is mainly within the range 2.96 $\pm$ 0.14 Å. It is thus centered around 2.96 Å found in $PtAl_2$.

The wide ranges of distances found in Pt_8Al_{21} are comparable to those found for several other complex structures formed by aluminium such as the Me_4Al_{13} compounds.[3]

As mentioned above the coordinations are higher in Pt_8Al_{21} than in $PtAl_2$. This indicates that the former structure is more densily packed than the latter. This is also convincingly demonstrated by the calculated mean atomic volumes of the phases in the platinum-aluminium system. (Mean atomic volume = cell volume divided by the number of atoms in the unit cell.) These are given in Fig. 3. This diagram diverges from the assumptions made by Huch and Klemm concerning the volumes of the aluminium rich phases of the platinum-aluminium system.

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