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The Crystal Structure of $Pu_{31}Pt_{20}$ and $Pu_{31}Rh_{20}$*

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$Pu_{31}Pt_{20}$ and $Pu_{31}Rh_{20}$ represent a new structural type for intermetallic compounds. The unit cell is tetragonal, space group $I4/mcm$, with $Z = 4$. For $Pu_{31}Pt_{20}$, $a = 11{\cdot}302$ (5), $c = 37{\cdot}388$ (23) Å; for $Pu_{31}Rh_{20}$, $a = 11{\cdot}076$ (4), $c = 36{\cdot}933$ (12) Å. This structure is closely related to the W_5Si_3 ($D8_m$) structure type. Data were collected on an automatic diffractometer and were corrected for absorption. The structure was solved by direct methods and refinement was by full-matrix least squares. For $Pu_{31}Pt_{20}$, $R_w = 0{\cdot}0535$ for 775 observed reflections and for $Pu_{31}Rh_{20}$, $R_w = 0{\cdot}0425$ for 890 observed reflections. All interatomic distances are within the normal range.

Introduction

The Pu–Pt phase diagram given by Kutaitsev, Chebotarev, Lebedev, Andrianov, Konev & Menshikova (1965) shows five intermetallic compounds: Pu_5Pt_3, PuPt, $PuPt_2$, $PuPt_3$ and $PuPt_5$. The above authors report that PuPt has the CrB (B_f) structure, $PuPt_2$ has the Cu_2Mg ($C15$) structure, and $PuPt_3$ has the $AuCu_3$ ($L1_2$) structure. Pu_5Pt_3 has the Mn_5Si_3 or $D8_8$ structure (Cromer & Larson, 1975) and the structure of $PuPt_5$ is still unknown. Roof (1976) has found that $PuPt_5$ does not have the common $CaCu_5$ structure. Roof (1976) has also found evidence for a compound believed to be $PuPt_4$. $Pu_{31}Pt_{20}$, the subject of the present paper, and $PuPt_4$ were not found by Kutaitsev *et al.* (1965).

Kutaitsev *et al.* (1965) also reported the Pu–Rh phase diagram. They found seven compounds: Pu_2Rh, Pu_5Rh_3, Pu_5Rh_4, PuRh and Pu_3Rh_4 all with unknown structures, and $PuRh_2$ with the Cu_2Mg structure and $PuRh_3$ with the $AuCu_3$ structure. The structure of Pu_5Rh_4 has been determined by Cromer (1977). In addition to the above compounds, $Pu_{31}Rh_{20}$ also exists and is isostructural with $Pu_{31}Pt_{20}$.

A preliminary account of the $Pu_{31}Pt_{20}$ structure was given by Cromer & Larson (1974) at a meeting of the American Crystallographic Association. At that time the formula of the phase was thought to be $Pu_{32}Pt_{19}$, but further work suggested that the probable formula was $Pu_{31}Pt_{20}$. A written account of this work was delayed in the hope that an isostructural compound would be found with one of the lighter Group VIII elements, so that the ideal formulation could be definitively determined. Such a compound has now been found with rhodium.

Alloy preparation

An alloy containing 37 at.% Pt was prepared by arc melting six times and then heat treating for 73 h at 1100 °C. This alloy had been made with the intention of preparing Pu_5Pt_3. Pu_5Pt_3 crystals were indeed found but, in addition, crystals having a large tetragonal cell and later identified as $Pu_{31}Pt_{20}$ were also present. An alloy containing 37 at.% Rh was similarly prepared and heat treated at 900 °C for 100 h. Several fragments were examined and all had the large tetragonal cell similar to the platinum compound. Crystals of Pu_5Rh_3 were not found, but could well have been present.

Data collection and processing

We would like at this time to give in some detail the procedures now used in this laboratory for intensity measurement, averaging of equivalent reflections and determining the weight of the average.

Intensities are measured with an automated Picker diffractometer and local versions of the orientation, least-squares and data-collection programs of Busing, Ellison, Levy, King & Roseberry (1968). A θ–2θ step-scan technique is used, usually with steps of 0·05° and a 2 s count for each step. The scan range is normally 2° (2θ) plus the α_1–α_2 dispersion. Background is counted for 10 times the single step time at each end of the range and is assumed to vary linearly within the range. Graphite-monochromated Mo $K\alpha$ radiation is normally used as the absorption coefficient of Pu for this radiation is lower than for any other convenient wavelength.

Heavy-metal intermetallic compounds present considerable problems because of high absorption and it is rare that a single-crystal fragment has a simple shape so that corrections can be accurately calculated.

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Consequently we normally collect a very redundant set of intensities, both to check on absorption corrections and to improve the accuracy of the unique data set by averaging.

Some terms for a single observation of the reflection *hkl* are defined: I = raw intensity count; B = background count; $C = 1/(\mathrm{Lp} \times t)$, where Lp is the Lorentz–polarization factor and t is the transmission factor; $F^2 = C(I - B)$ = structure factor squared; k = empirical constant combining systematic errors such as instrumental instability; $\sigma^2(F^2) = [C(I + B) + k^2F^4]$ = variance of F^2; $s^2(F^2) = [C(I + B)]$ = variance of F^2 due to counting statistics only; $T_{\min}$ = threshold parameter for observed reflections; a reflection is considered observed if $F^2 \geq T_{\min}\sigma(F^2)$. When n equivalent reflections are measured the weighted average, $\overline{F^2}$, is calculated as

$$\overline{F^2} = \sum_{i=1}^{n} \frac{F_i^2}{\sigma^2(F_i^2)} \Bigg/ \sum_{i=1}^{n} \frac{1}{\sigma^2(F_i^2)} . \qquad (1)$$

The variance of $\overline{F^2}$ is

$$\sigma^2(\overline{F^2}) = \frac{1}{\sum\limits_{i=1}^{n} \dfrac{1}{s^2(F_i^2)}} + k^2 \frac{\sum\limits_{i=1}^{n} F_i^4}{n} . \qquad (2)$$

The average structure factor $\bar{F}$ is $|\overline{F^2}|^{1/2}$ and $\sigma(\bar{F}) = \sigma(\overline{F^2})/(2|\bar{F}|)$. One can also estimate $\sigma^2(\overline{F^2})$ from:

$$\sigma^2(\overline{F^2}) = \left[\frac{1}{n(n-1)} \sum_{i=1}^{n} (F_i^2 - \overline{F^2})^2\right] . \qquad (3)$$

In practice we compute $\sigma^2(\overline{F^2})$ both ways and here have used the larger of the two in the manner of Corfield, Doedens & Ibers (1967) to compute $w(\bar{F})$, the weight of $\bar{F}$: $w(\bar{F}) = 4\overline{F^2}/\sigma^2(\overline{F^2})$.

In the calculation of $\overline{F^2}$ all F_i^2 are used, even though some might be accidentally negative. If $\overline{F^2}$ is less than $T_{\min}\sigma(\overline{F^2})$, then $\bar{F} = -[T_{\min}\sigma(\overline{F^2})]^{1/2}$. The negative sign is a flag to omit this particular reflection in subsequent least-squares refinement. In the listings of observed and calculated structure factors the negative sign means that the observed quantity is less than the stated value.

The observed values of F^2 and $\overline{F^2}$ are preserved and not set to a threshold value. In our procedure, if a least-squares refinement is made which minimizes $\Sigma\, w(F_o^2 - F_c^2)^2$, all data are used at their observed values, even if accidentally negative.

In the program which averages the equivalent reflections, certain statistics are computed which give an indication of the overall agreement between equivalent reflections. These are weighted sums over F and F^2 and are defined below:

$$R_F = \sum_{j=1}^{N} \sum_{i=1}^{n_j} w(F_{i,j})|\bar{F}_j - F_{i,j}| / \sum_{j=1}^{N} n_j w(\bar{F}_j)\bar{F}_j , \qquad (4)$$

$$R_F^2 = \sum_{j=1}^{N} \sum_{i=1}^{n_j} w(F_{i,j}^2)|\overline{F_j^2} - F_{i,j}^2| / \sum_{j=1}^{N} n_j w(\overline{F_j^2})\overline{F_j^2} . \qquad (5)$$

In the above, the w's are the appropriate $1/\sigma^2$, and the summations are over the N unique reflections, each having been observed n_j times ($n_j > 1$). Only observed data are used in these sums. These statistics are useful for assessing the validity of absorption corrections and R_F gives an estimate of the final R_w.

Equation (2) is similar in form to that given by Abrahams (1964) in that the instrumental part of the variance of $\overline{F^2}$ is separated from the variance due to counting statistics. A derivation of equation (2) has been given by Ryan (1977).

Crystallographic data for the two compounds, and information pertinent to the data collection and reduction, are given in Tables 1 and 2. Preliminary precession photographs had shown that the space group, if centrosymmetric, is *I*4/*mcm*. Reflections *hkl* were present only for $h + k + l = 2n$ and reflections *h*0*l* were present only for $h = 2n$ and $l = 2n$. The reason for the smaller number of reflections for $Pu_{31}Pt_{20}$ is that some of the data were accidentally lost because of torn paper tapes and parity errors.

Absorption corrections were made both empirically (Furnas, 1957) and by the analytic method of de Meulenaer & Tompa (1965). The latter corrections used a program obtained from Dr L. Templeton. The shape of the $Pu_{31}Pt_{20}$ crystal was approximated by seven plane faces, and six plane faces were used to approximate the shape of the $Pu_{31}Rh_{20}$ crystal. It can be seen in Table 2 that the empirical corrections, although not as good as the analytic corrections, do a reasonably good job. In fact it is not often that we have a crystal with a shape that can be defined well enough so that analytic corrections are better than empirical corrections. The data sets with analytic absorption corrections were those used in the final analyses.

Table 1. *Crystallographic data for* $Pu_{31}Pt_{20}$ *and* $Pu_{31}Rh_{20}$

	$Pu_{31}Pt_{20}$	$Pu_{31}Rh_{20}$
Space group	*I*4/*mcm*	*I*4/*mcm*
a ($\lambda = 0{\cdot}70930$ Å)	11·302 (5) Å	11·076 (4) Å
c	37·388 (23)	36·933 (12)
Z	4	4
d_{calc}	15·73 g cm^{-3}	13·87 g cm^{-3}
d_{meas} (of ingot)	15·55	13·79
μ	1127 cm^{-1}	600 cm^{-1}

Table 2. *Data collection and reduction*

	$Pu_{31}Pt_{20}$	$Pu_{31}Rh_{20}$
Radiation	Mo $K\alpha$ (graphite-monochromated)	Mo $K\alpha$ (graphite-monochromated)
$2\theta_{max}$	50°	50°
Take-off angle	3°	3°
Step size	0·05°	0·05°
Step time	2 s	2 s
Scan range	2°	2°
T_{min} (threshold parameter)	2·0	2·0
Number of reflections	2852	4020
Unique reflections	1029	1113
Unique reflections observed	775	890
Reflections measured once	73	9
Reflections measured twice	451	198
Reflections measured three times	143	9
Reflections measured four times	362	897
R_F (no corrections)	0·099	0·085
R_F (empirical corrections)	0·047	0·045
R_F (analytic corrections)	0·031	0·039
Minimum transmission (analytic corrections)	0·020	0·078
Maximum transmission (analytic corrections)	0·172	0·222
Crystal volume	0·120 mm^3	0·168 mm^3

Determination of the structure

A geometric relation was first noted between the large tetragonal cell of the platinum compound and the tetragonal cell of Pu_5Ru_3 (Cromer, Larson & Roof, 1975), a compound with about the same stoichiometry and with the same space group. The *a* axes are about the same and the *c* axes differ by a factor of about seven. The small cell has the W_5Si_3 or $D8_m$ structure type and in this structure there are large atoms at $0,\frac{1}{2},\frac{1}{4}$ which are somewhat crowded. A model was tried having seven small cells stacked in the **c** direction but with only 12 instead of 14 large atoms spread out along $0,\frac{1}{2},z$. This model, based on an ordering of the disorder found in $(Pu,Ce)_5Co_3$ (Larson, Roof & Cromer, 1964), did not refine.

We then applied direct methods, for the centrosymmetric space group *I*4/*mcm*, and easily found the positions of all the atoms, but were uncertain which atom was in which site. In fact, least-squares refinements were about the same no matter how the sites were occupied, even if all atoms were called plutonium. After correction for anomalous dispersion, the Pu and Pt scattering factors differ by only 5 or 6% in the region which has most of the data. Consequently the behavior of thermal parameters could not be used to identify the site occupancy. (In retrospect, the final correct model did give a smaller sum of residuals than any other model.)

The atoms were then identified according to the number of neighbors in each site and by the relation of this structure to that of the small tetragonal cell. The atom at 0,0,0 was first thought to be Pu but was later correctly identified as Pt.

About two years after most of the work on $Pu_{31}Pt_{20}$ was done, the same phase was found with rhodium. In this compound the difference in scattering power is so great that there is no ambiguity and the structure as originally deduced was shown to be correct.

Least-squares refinement, with anisotropic thermal parameters, led to the results shown in Tables 3 and 4.* Refinement minimized $\Sigma\, w(\Delta F)^2$ and used relativistic

Table 3. *Final positional parameters for* $Pu_{31}Pt_{20}$

	Equipoint	x	y	z
Pu(1)	4(*b*)	0	$\frac{1}{2}$	$\frac{1}{4}$
Pu(2)	8(*g*)	0	$\frac{1}{2}$	0·0758 (1)
Pu(3)	8(*g*)	0	$\frac{1}{2}$	0·1655 (1)
Pu(4)	8(*h*)	0·1576 (3)	$x+\frac{1}{2}$	0
Pu(5)	32(*m*)	0·2964 (2)	0·4310 (2)	0·0509 (1)
Pu(6)	32(*m*)	0·2851 (2)	0·5774 (2)	0·1336 (1)
Pu(7)	32(*m*)	0·2804 (2)	0·4118 (2)	0·2123 (1)
Pt(1)	4(*c*)	0	0	0
Pt(2)	4(*a*)	0	0	$\frac{1}{4}$
Pt(3)	8(*f*)	0	0	0·0983 (1)
Pt(4)	8(*f*)	0	0	0·1762 (1)
Pt(5)	8(*h*)	0·4021 (3)	$x+\frac{1}{2}$	0
Pt(6)	16(*l*)	0·1825 (2)	$x+\frac{1}{2}$	0·0742 (1)
Pt(7)	16(*l*)	0·3416 (2)	$x+\frac{1}{2}$	0·1258 (1)
Pt(8)	16(*l*)	0·1549 (2)	$x+\frac{1}{2}$	0·2101 (1)

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* Lists of the final least-squares cycle, structure factors, anisotropic thermal parameters and interatomic-distance, thermal-ellipsoid and polyhedron calculations for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32510 (115 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. *Final positional parameters for* $Pu_{31}Rh_{20}$

	Equipoint	x	y	z
Pu(1)	4(*b*)	0	$\frac{1}{2}$	$\frac{1}{4}$
Pu(2)	8(*g*)	0	$\frac{1}{2}$	0·0756 (1)
Pu(3)	8(*g*)	0	$\frac{1}{2}$	0·1656 (1)
Pu(4)	8(*h*)	0·1586 (1)	$x+\frac{1}{2}$	0
Pu(5)	32(*m*)	0·2947 (1)	0·4299 (1)	0·0500 (1)
Pu(6)	32(*m*)	0·2855 (1)	0·5774 (1)	0·1346 (1)
Pu(7)	32(*m*)	0·2819 (1)	0·4125 (1)	0·2114 (1)
Rh(1)	4(*c*)	0	0	0
Rh(2)	4(*a*)	0	0	$\frac{1}{4}$
Rh(3)	8(*f*)	0	0	0·0940 (1)
Rh(4)	8(*f*)	0	0	0·1734 (1)
Rh(5)	8(*h*)	0·4035 (3)	$x+\frac{1}{2}$	0
Rh(6)	16(*l*)	0·1812 (2)	$x+\frac{1}{2}$	0·0726 (1)
Rh(7)	16(*l*)	0·3417 (3)	$x+\frac{1}{2}$	0·1269 (1)
Rh(8)	16(*l*)	0·1536 (2)	$x+\frac{1}{2}$	0·2109 (1)

Hartree–Fock scattering factors (Cromer & Waber, 1974) and the anomalous-dispersion terms of Cromer & Liberman (1970). $R = \Sigma|\Delta F|/\Sigma F_o$ and $R_w = [\Sigma w(\Delta F)^2/\Sigma wF_o^2]^{1/2}$, with unobserved reflections omitted, were 0·0574 and 0·0535 for $Pu_{31}Pt_{20}$ and 0·0468 and 0·0425 for $Pu_{31}Rh_{20}$. The goodness of fit was 2·05 for the Pt compound and 1·55 for the Rh compound. No large or very anisotropic thermal parameters are present and thus no substitutional or positional disorder is indicated.

Discussion

$Pu_{31}Pt_{20}$ and $Pu_{31}Rh_{20}$ represent a new structure type but are closely related to Pu_5Ru_3, which has the W_5Si_3 ($D8_m$) type. Fig. 1 shows one-half of the $Pu_{31}Pt_{20}$ cell and four cells of Pu_5Ru_3 projected along their y axes. Only half of the large cell need be shown as there is a mirror at $z = \frac{1}{4}$. The y coordinates are shown beside each circle. The atoms of $Pu_{31}Pt_{20}$ at $z = \frac{1}{4}$ and in the layers at either side of $z = \frac{1}{4}$ have virtually the same coordinates as those in Pu_5Ru_3. However, the smaller atoms in these layers are displaced slightly and are not coplanar with the large atoms as in Pu_5Ru_3. The second and third layers either side of $z = \frac{1}{4}$ in $Pu_{31}Pt_{20}$ become progressively more distorted and the small atoms are further from the plane of the large atoms. The fourth

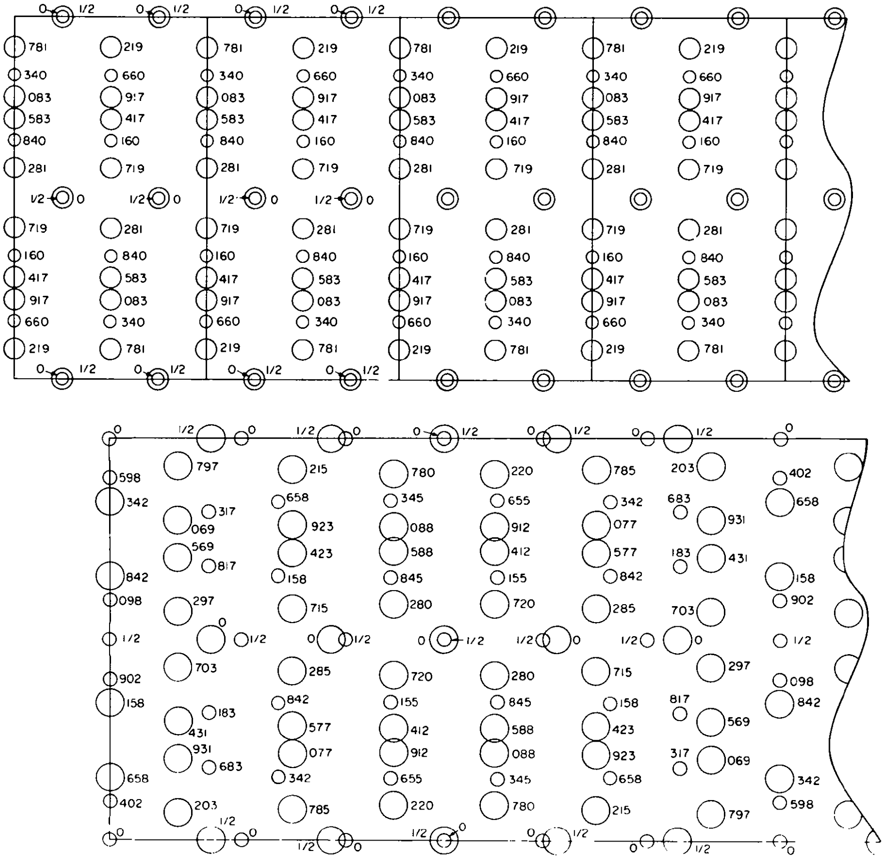

Fig. 1. The lower half of the figure shows $\frac{1}{2}$ of the $Pu_{31}Pt_{20}$ cell projected along y and the upper half shows four cells of Pu_5Ru_3 projected along y. x is vertical and z horizontal. The y coordinates are shown adjacent to each circle. The large circles are Pu and the small circles are the Group VIII elements.

layer, now at $z = 0$, bears little relation to the original, small cell. The large cell has 16 fewer Pu atoms and four fewer Group VIII atoms than do seven of the small cells. In seven small cells there are 14 Pt atoms along $0,0,z$ and 14 Pu atoms along $0,\frac{1}{2},z$. In the large cell there are 12 Pt atoms along $0,0,z$ (and $\frac{1}{2},\frac{1}{2},z$) and 10 Pu atoms along $0,\frac{1}{2},z$ (and $\frac{1}{2},0,z$). The layers at $z = 0, \frac{1}{2}$ in the large cell have only 4 Pu atoms whereas the corresponding layers in the small cell have 8 Pu atoms. One Pt atom is added to the $z = 0, \frac{1}{2}$ layers in the large cell.

The distances to the neighbors of each atom are given in Table 5. No distances are unusually short. All Pu–Pu and Pu–X distances are shorter in $Pu_{31}Rh_{20}$, but most of the X–X distances are larger in this

Table 5. *Interatomic distances* (Å) *in* $Pu_{31}X_{20}$ *compounds*

The first distance is for X = Pt and the second for X = Rh. Each pair is for structurally equivalent distances.

Pu(1)–2Pu(3)	3·161 (5)	3·116 (2)
–8Pu(7)	3·608 (2)	3·567 (2)
–4*X*(8)	2·890 (3)	2·805 (3)
Pu(2)–Pu(3)	3·352 (7)	3·326 (3)
–2Pu(4)	3·791 (5)	3·737 (2)
–4Pu(5)	3·563 (3)	3·486 (2)
–4Pu(6)	4·039 (4)	3·936 (2)
–2*X*(5)	3·237 (5)	3·174 (3)
–2*X*(6)	2·918 (3)	2·841 (4)
–2*X*(7)	3·147 (5)	3·121 (4)
Pu(3)–Pu(1)	3·161 (5)	3·116 (2)
–Pu(2)	3·352 (7)	3·326 (3)
–4Pu(6)	3·509 (3)	3·470 (2)
–4Pu(7)	3·756 (3)	3·680 (2)
–2*X*(7)	2·934 (4)	2·862 (4)
–2*X*(8)	2·986 (4)	2·930 (4)
Pu(4)–2Pu(2)	3·791 (5)	3·737 (2)
–4Pu(5)	3·555 (3)	3·478 (2)
–4Pu(5)	3·666 (4)	3·564 (2)
–2*X*(1)	4·260 (2)	4·169 (2)
–2*X*(5)	2·965 (4)	2·909 (4)
–*X*(5)	3·909 (6)	3·835 (6)
–2*X*(6)	2·803 (4)	2·706 (3)
Pu(5)–Pu(2)	3·563 (3)	3·486 (2)
–Pu(4)	3·555 (3)	3·478 (2)
–Pu(4)	3·666 (4)	3·564 (2)
–2Pu(5)	3·436 (3)	3·398 (2)
–Pu(5)	3·634 (4)	3·518 (3)
–Pu(5)	3·805 (5)	3·692 (2)
–Pu(6)	3·608 (3)	3·529 (2)
–Pu(6)	3·875 (3)	3·787 (2)
–*X*(1)	3·086 (2)	3·030 (1)
–*X*(3)	3·007 (4)	2·900 (3)
–*X*(5)	2·960 (3)	2·883 (3)
–*X*(6)	2·950 (3)	2·891 (3)
–*X*(6)	3·240 (3)	3·167 (2)
–*X*(7)	3·361 (4)	3·363 (3)
Pu(6)–Pu(2)	4·039 (4)	3·936 (2)
–Pu(3)	3·509 (3)	3·470 (2)
–Pu(5)	3·608 (4)	3·529 (2)
–Pu(5)	3·875 (3)	3·787 (2)
–Pu(6)	3·320 (4)	3·260 (3)
–2Pu(6)	3·651 (3)	3·572 (2)
–Pu(7)	3·395 (3)	3·372 (2)
–Pu(7)	3·557 (3)	3·527 (2)
–*X*(3)	2·952 (4)	2·939 (3)
–*X*(4)	2·977 (4)	2·903 (3)
–*X*(6)	2·862 (4)	2·811 (3)
–*X*(7)	3·052 (3)	2·980 (2)
–*X*(7)	3·080 (4)	3·007 (4)
–*X*(8)	3·239 (4)	3·283 (3)
Pu(7)–Pu(1)	3·608 (2)	3·567 (2)
–Pu(3)	3·756 (3)	3·680 (2)
–Pu(6)	3·395 (3)	3·372 (2)
–Pu(6)	3·557 (3)	3·527 (2)
–Pu(7)	3·072 (4)	3·045 (2)
–Pu(7)	3·451 (5)	3·449 (2)
–Pu(7)	3·514 (5)	3·510 (2)
–2Pu(7)	3·783 (3)	3·681 (2)
–*X*(2)	3·023 (2)	2·968 (1)
–*X*(4)	2·996 (3)	2·956 (2)
–*X*(7)	3·605 (5)	3·496 (3)
–*X*(8)	2·996 (3)	2·956 (3)
–*X*(8)	3·093 (3)	3·025 (2)
–*X*(8)	3·315 (4)	3·285 (3)
X(1)–4Pu(4)	4·260 (2)	4·169 (2)
–8Pu(5)	3·086 (2)	3·030 (1)
–2*X*(3)	3·675 (6)	3·470 (5)
X(2)–8Pu(7)	3·023 (2)	2·968 (1)
–2*X*(4)	2·759 (6)	2·828 (4)
X(3)–4Pu(5)	3·007 (4)	2·900 (3)
–4Pu(6)	2·952 (4)	2·939 (3)
–*X*(1)	3·675 (6)	3·471 (5)
–*X*(4)	2·913 (8)	2·934 (6)
X(4)–4Pu(6)	2·977 (4)	2·903 (3)
–4Pu(7)	2·996 (3)	2·956 (2)
–*X*(2)	2·759 (6)	2·828 (4)
–*X*(3)	2·913 (8)	2·934 (6)
X(5)–2Pu(2)	3·237 (5)	3·174 (3)
–2Pu(4)	2·965 (4)	2·909 (4)
–Pu(4)	3·909 (6)	3·835 (6)
–4Pu(5)	2·960 (3)	2·883 (3)
–*X*(5)	3·129 (9)	3·024 (10)
X(6)–Pu(2)	2·918 (3)	2·841 (4)
–Pu(4)	2·803 (4)	2·706 (3)
–2Pu(5)	2·950 (3)	2·891 (3)
–2Pu(5)	3·240 (3)	3·167 (2)
–2Pu(6)	2·862 (4)	2·811 (3)
–*X*(7)	3·192 (5)	3·215 (5)
X(7)–Pu(2)	3·147 (5)	3·121 (4)
–Pu(3)	2·934 (4)	2·862 (4)
–2Pu(5)	3·361 (4)	3·363 (3)
–2Pu(6)	3·052 (3)	2·980 (2)
–2Pu(6)	3·080 (4)	3·007 (4)
–2Pu(7)	3·605 (5)	3·496 (3)
–*X*(6)	3·192 (5)	3·215 (5)
–*X*(8)	4·341 (5)	4·279 (5)
X(8)–Pu(1)	2·890 (3)	2·805 (3)
–Pu(3)	2·986 (4)	2·930 (4)
–2Pu(6)	3·239 (4)	3·283 (3)
–2Pu(7)	2·996 (3)	2·956 (3)
–2Pu(7)	3·093 (3)	3·025 (2)
–2Pu(7)	3·315 (4)	3·285 (3)
–*X*(7)	4·341 (5)	4·279 (5)
–*X*(8)	4·260 (6)	4·179 (7)

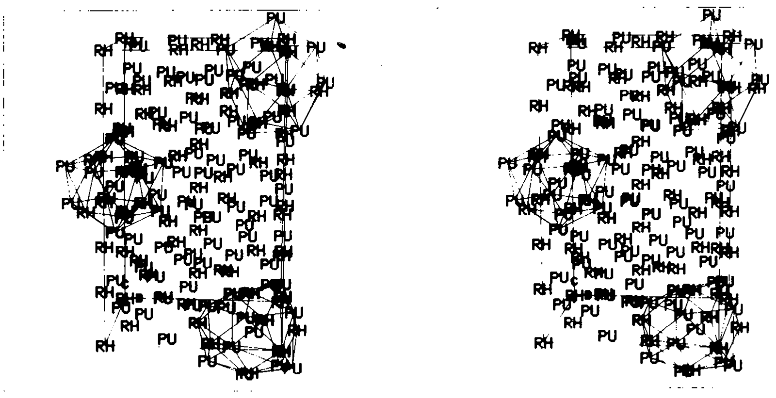

Fig. 2. One-half the unit cell of $Pu_{31}Rh_{20}$, from $z = 0$ to $z = \frac{1}{2}$. The view vector is approximately along x. The origin is at the lower left rear. Polyhedra shown are Pu(1) at $\frac{1}{2},0,\frac{1}{4}$ on the left, Pu(4) at 0·659,0·841,0 at the bottom right and Pu(5) at 0·795,0·930,0·450 at the top.

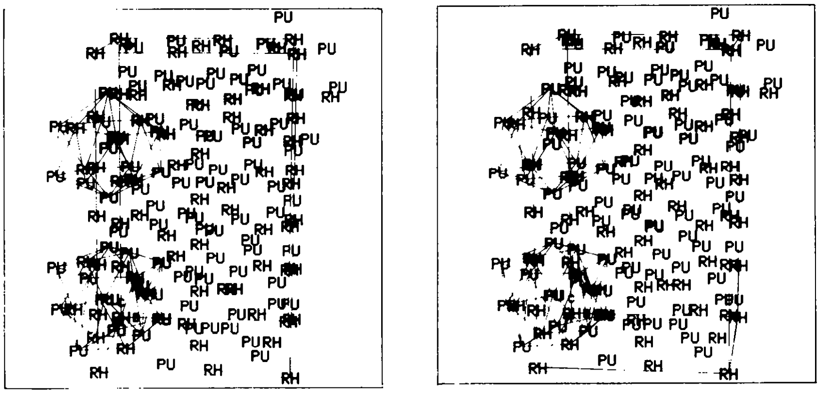

Fig. 3. Pu(2) at $\frac{1}{2}$,0,0·076 is the lower polyhedron and Pu(3) at $\frac{1}{2}$,0,0·334 is the upper polyhedron.

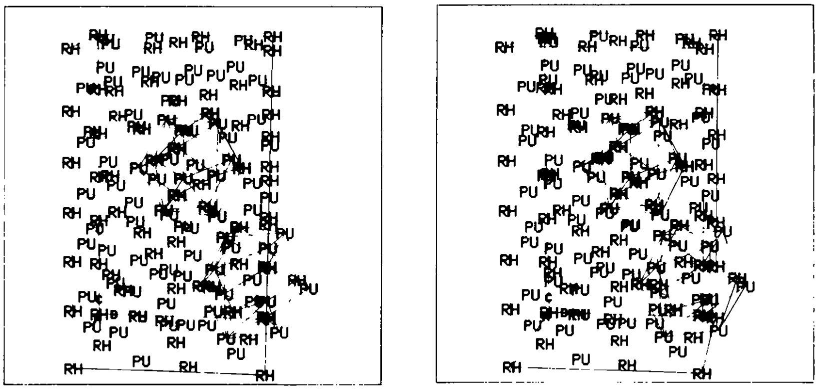

Fig. 4. Pu(6) at 0·786,0·923,0·135 (lower) and Pu(7) at 0·282,0·588,0·289 (upper).

compound. If the midpoint between two atoms is closer to these two atoms than to any other atom, the two atoms are defined as neighbors. This definition of neighbor is, in effect, the same as that given by Frank & Kasper (1958) who define as neighbors two atoms which share a common domain face. The convex polyhedra formed by these neighbors are shown in Figs. 2–7.

In the following discussion we will refer to M and X as in $M_{31}X_{20}$. $M(1)$ and $M(3)$ have four X and twelve M neighbors. A distorted hexagon of four M and two X atoms is on either side of the central M atom in an

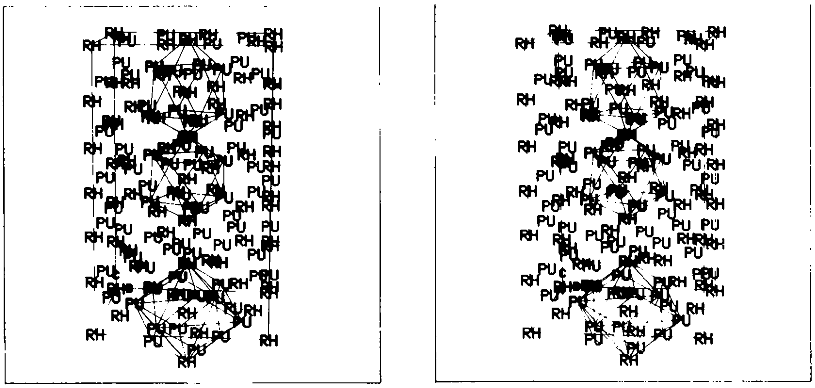

Fig. 5. Rh(1) at ½,½,0 (lower), Rh(2) at ½,½,¼ (middle) and Rh(3) at ½,½,0·406 (upper).

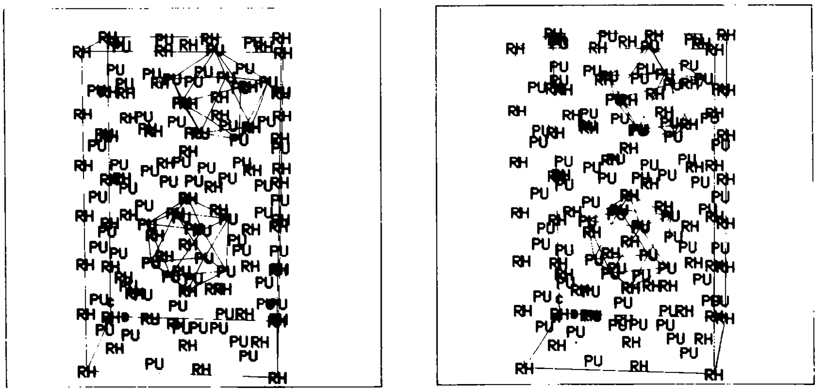

Fig. 6. Rh(4) at ½,½,0·173 (lower) and Rh(6) at 0·819,0·681,0·427 (upper).

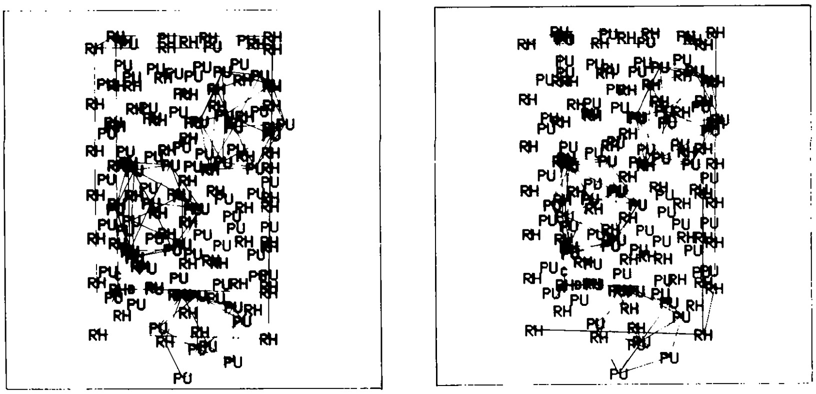

Fig. 7. Rh(5) at 0·903,0·597,0 (lower), Rh(7) at 0·658,0·842,0·373 (upper) and Rh(8) at 0·846,0·346,0·211 (middle).

antiprism configuration and each hexagon is capped by another M neighbor. The $M(1)$ polyhedron is exactly like Pu(1) in the Pu_5Ru_3 ($D8_m$) structure, but for $M(3)$, which has a lower point symmetry, the two hexagonal rings and the caps are not equidistant. Nevertheless these two polyhedra are topologically the same. $M(2)$ is further away from $z = \frac{1}{4}$ where the structure is most like that of the $D8_m$ type. $M(2)$ again has two hexagonal rings on either side but while the top ring is capped by a single M atom the lower ring is capped by four atoms. $M(2)$ has eleven M and six X neighbors.

$M(4)$ has seven X and ten M neighbours. These are arranged in three pentagonal layers, one X atom coplanar with $M(4)$ at $z = 0$, and two layers of M atoms above and below. This complex is capped with X atoms at each end.

$M(5)$, $M(6)$ and $M(7)$, which are in general positions, each have six X and nine M neighbors and the polyhedra are similar to that of Pu(2) in Pu_5Rh_3 in terms of the number and kinds of neighbors. The $M(6)$ and $M(7)$ polyhedra can be described as formed by a somewhat puckered ring of six atoms on either side of the central atom, with one ring being capped by one atom and the other ring capped by two atoms. The polyhedron of $M(5)$ is not easily described. However, there is a puckered ring of six atoms approximately coplanar with $M(5)$. On one side is a puckered ring of four atoms and on the other side a planar array of four atoms with this plane capped by a single atom.

$X(1)$ has two X and twelve M neighbors. Eight M neighbors are at the corners of a cube, four more M neighbors are coplanar with $M(1)$ at $z = 0$ and two X neighbors cap this arrangement. $X(2)$, $X(3)$ and $X(4)$ each have two X and eight M neighbors and are like Ru(1) in Pu_5Ru_3. The eight M neighbors form an antiprism and the X atoms cap the ends of this antiprism. $X(5)$ has a similar polyhedron but only one of the end atoms is X so that there are nine M neighbors and one X. $M(6)$ has one X and eight M neighbors which form a somewhat distorted antiprism with the Pt atom at one end. $M(7)$ and $M(8)$ have two X and ten M neighbors which form somewhat distorted icosohedra.

We wish to thank Dr R. R. Ryan for many helpful discussions concerning the averaging of equivalent reflections, and V. O. Struebing for preparation of the alloys.

Addendum: – A recent paper by Moreau, Paccard & Parthé (1976) on the structure of Y_3Rh_2 has just come to our attention. Y_3Rh_2 has a structure closely related to that of Pu_5Ru_3 and the present structure. To see the relation between Y_3Rh_2 and $Pu_{31}Rh_{20}$, look again at Fig. 1. The arrangement at $z = \frac{1}{4}$ and the first layer on either side of $z = \frac{1}{4}$ is virtually identical in these two structures and in the parent small cell. In the second layer from $z = \frac{1}{4}$: in $Pu_{31}Rh_{20}$ the smaller atoms are displaced away from $z = \frac{1}{4}$ and in Y_3Rh_2 the smaller atoms are displaced toward $z = \frac{1}{4}$. The third layer from $z = \frac{1}{4}$, which is in the $Pu_{31}Rh_{20}$ structure, does not exist in Y_3Rh_2. The next layers, at $z = 0$ and $z = \frac{1}{2}$, are interchanged in Y_3Rh_2. That is, the $z = 0$ layer in $Pu_{31}Rh_{20}$ is virtually identical with the $z = \frac{1}{2}$ layer in Y_3Rh_2. In effect, eight units of M_5X_3 (two unit cells) have been removed from the $M_{31}X_{20}$ cell, leaving 28 units of M_3X_2.

The correspondence between the polyhedra in Y_3Rh_2 and $M_{31}X_{20}$ is given below:

$Y(1) \simeq M(5–7)$
$Y(2) \simeq M(5–7)$
$Y(3) \simeq M(4)$
$Y(4) \simeq M(2)$
$Y(5) \simeq M(1)$

$Rh(1) \simeq X(6)$
$Rh(2) \simeq X(7–8)$
$Rh(3) \simeq X(5)$
$Rh(4) \simeq X(2–4)$
$Rh(5) \simeq X(1)$
$Rh(6) \simeq X(2–4)$.

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