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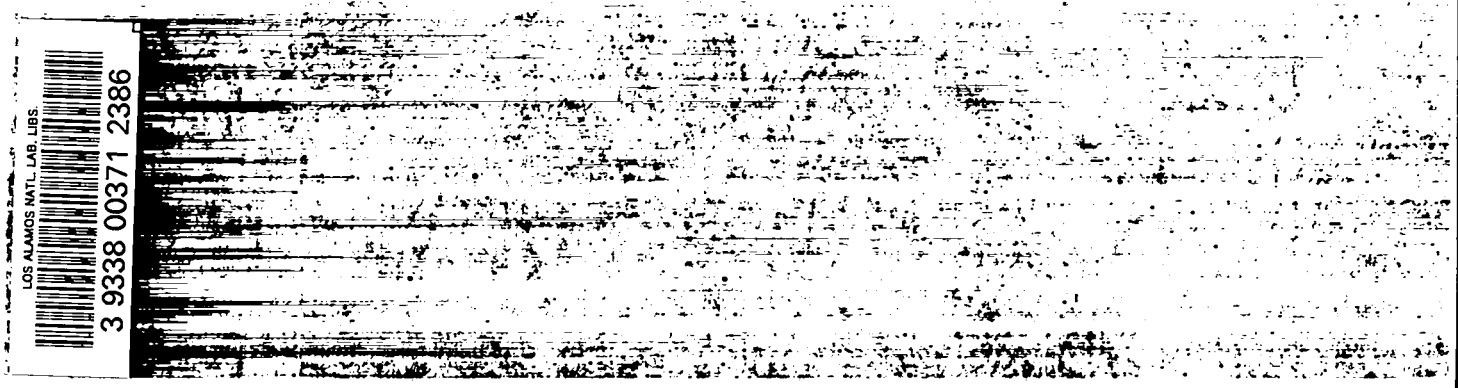
A NEUTRON DIFFRACTION EXAMINATION OF ALPHA PLUTONIUM AT 23 °K



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A NEUTRON DIFFRACTION EXAMINATION OF ALPHA PLUTONIUM AT 23 °K

by

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ABSTRACT

A neutron diffraction pattern obtained by the transmission method from a thin slab of Pu at 23 °K has been analyzed in terms of an analytical expression consisting of the summation of Gaussian peaks. The angular positions of the Gaussian peaks have been indexed in terms of a monoclinic unit cell which compares favorably with the room temperature cell given by Zachariasen. The intensities of the Gaussian peaks yield a structure essentially in agreement with the room temperature structure but with the important differences of a reduction in the average number of neighbors from 14 at room temperature to 12.5 at the low temperature, indicating a tendency of the atoms to cluster; and a reduction in the gross average Pu-Pu interatomic distance from 3.19 Å at room temperature to 3.16 at the low temperature. This small contraction in the average distance is not significant, however, because of the rather large standard deviations observed for the individual interatomic distances.

CONTENTS

INTRODUCTION

The primary purpose of the investigation described in this report was to ascertain whether or not a gross crystallographic structural change that could be correlated with other anomalous properties occurs in α-Pu at low temperatures. Neutron diffraction was chosen for the investigation. For the more conventional X-ray diffraction, knowledge of the change in scattering amplitude with the diffraction angle for Pu is required. But in neutron diffraction, since the size of the nucleus is very small in comparison with the neutron wavelength, the scattering amplitude does not change with diffraction angle and is constant over the experimental range of 2θ. Also, at the low temperature used in the investigation the thermal vibrations of the atoms are small enough to be considered negligible and therefore can be eliminated as the variables in the structural analysis.

EXPERIMENTAL RESULTS

The experimental sample consisted of a slab of α-Pu approximately 2 inches square and 0.005 inch thick machined from a cast billet. During cooling from the liquid state to room temperature, Pu passes through six phase transformations, a process which imparts a very small grain size to the sample. Experimental work on similar specimens prepared in this manner indicates that they are free from preferred orientation (Waber, 1963).

After being encased in an aluminum sample holder, the Pu was examined by neutron diffraction (transmission method). Spectrometer #2 of the Omega West Reactor of the Los Alamos Scientific Laboratory was used, and the neutron wavelength was 1.3918 Å. A trace of the neutron diffraction pattern obtained by G. P. Arnold and N. G. Nereson, both of the Los Alamos Scientific Laboratory, is given in Fig. 1.

EXPERIMENTAL ANALYSIS

Since the mechanical resolution of the diffraction pattern is rather poor (as shown in Fig. 1), it was decided to determine a mathematical resolution of the pattern by using the following analytical expression. The neutron diffraction peaks are assumed to be Gaussian and

$$Y = \text{Background} + \sum_{n=1}^{N} \frac{I_n}{w_n\sqrt{2\pi}} \exp\left[-\frac{1}{2}(x - b_n)^2/w_n^2\right] \qquad (1)$$

where

Y = number of neutron counts

N = number of peaks in one neutron diffraction pattern

I_n = area (or intensity) of one diffraction peak

w_n = a half-width for each peak

b_n = midpoint of each peak

$x = 2\theta$

This expression consists of a background term plus the summation of a number of Gaussian peaks. This equation was programmed for the

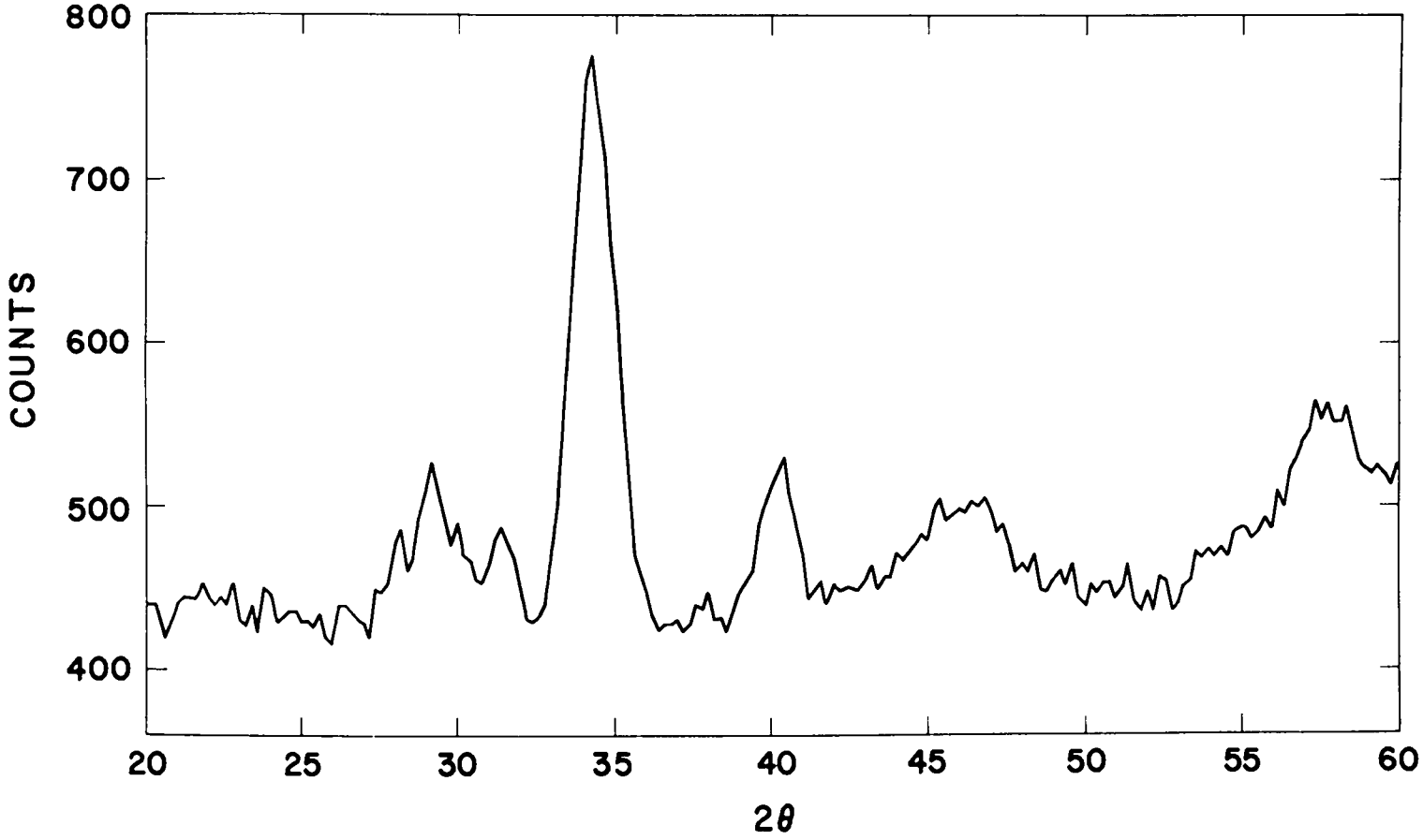

Fig. 1. Experimental neutron diffraction pattern for α-Pu at 23 °K

MANIAC computer by A. L. Bowman and for the IBM 7030 computer (STRETCH) by R. Engleman, both of the Los Alamos Scientific Laboratory, so that a least-squares solution could be obtained for the background, I_n, and b_n. Preliminary results from the MANIAC were used in the STRETCH program to determine that the experimental pattern of Fig. 1 could be represented by a background term and the summation of 24 Gaussian peaks. The neutron diffraction pattern calculated from the Gaussian analytical expression of Eq. (1) is given in Fig. 2. The least-squares values of the background, I_n, and b_n used for this calculation are given in Table 1. The half-width, w_n, is a function of the 2θ angle, b_n, and therefore is not a variable in the present least-squares analysis. The values of w_n used, also given in Table 1, were calculated from the following expression:

$$w_n = k_0 + k_1 \tan \theta_n + k_2 \tan^2 \theta_n \qquad (2)$$

where $k_0 = 0.1555 \pm 0.0492$, $k_1 = -1.0238 \pm 0.2448$, $k_2 = 3.3937 \pm 0.2855$. The general form of this expression (a polynomial in $\tan \theta_n$) and the signs of k_0, k_1, and k_2 were theoretically determined by Caglioti, Paoletti, and Ricci (1958). The numerical values of k_0, k_1, and k_2 were determined for spectrometer #2 of the Omega West Reactor by examining Ni, V_2C, and TaN samples with the Gaussian summation equation [Eq. (1)]. For these samples, for which the mechanical resolution is quite good, the half-width term was allowed to be a least-squares variable. After the w_n obtained was plotted against $\tan \theta_n$ for these specimens, the

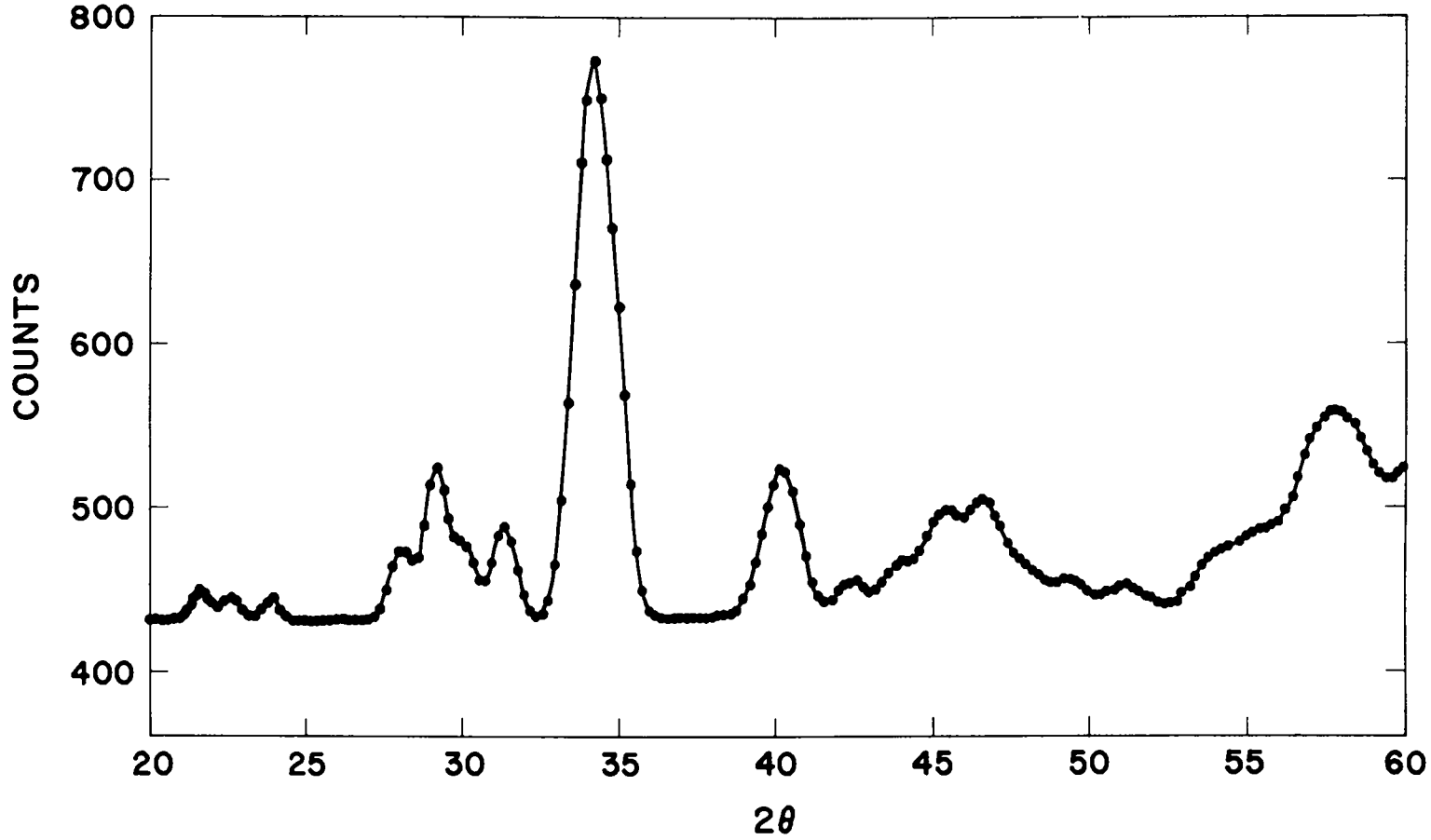

Fig. 2. Calculated neutron diffraction pattern for α-Pu at 23 °K, based on Eq. (1)

Table 1. VALUES OF N, I_n, w_n, AND b_n DERIVED BY USING THE GAUSSIAN SUMMATION EQUATION.

Assigned indices hkℓ for α-Pu at 23 °K are also listed.

N	I_n	w_n	b_n	Assigned Indices hkℓ
1	13.48 ± 2.02	0.2894	21.627 ± 0.351	110,11-1,102
2	10.35 ± 2.03	0.2939	22.581 ± 0.406	003,012
3	7.71 ± 2.03	0.3015	23.924 ± 0.464	10-3,111,11-2
4	37.37 ± 2.10	0.3342	28.073 ± 0.238	112,20-2,013,103
5	78.94 ± 2.20	0.3447	29.158 ± 0.186	11-3,201
6	40.81 ± 2.22	0.3542	30.085 ± 0.258	004,10-4
7	51.56 ± 2.15	0.3685	31.388 ± 0.211	20-3,21-1,210
8	120.82 ± 6.85	0.3956	33.675 ± 0.318	21-2,113,202,211
9	256.80 ± 5.76	0.4021	34.195 ± 0.297	020,014
10	163.99 ± 4.51	0.4113	34.917 ± 0.223	11-4,021
11	41.85 ± 5.51	0.4791	39.793 ± 0.521	203,114,30-1
12	89.65 ± 5.50	0.4883	40.415 ± 0.370	21-4,30-2,300,122,023,11-5
13	25.81 ± 2.43	0.5182	42.371 ± 0.426	015,20-5,12-3,30-3,213,105,301
14	39.91 ± 2.64	0.5421	43.889 ± 0.415	31-1,22-1,220,31-2,310,22-2
15	83.44 ± 2.87	0.5645	45.270 ± 0.346	10-6,204,123,21-5,221,30-4,006
16	95.23 ± 3.26	0.5870	46.625 ± 0.387	31-3,024,12-4,115,311,302,22-3
17	40.40 ± 3.32	0.6076	47.847 ± 0.590	20-6,11-6,214,222
18	34.59 ± 2.84	0.6338	49.359 ± 0.521	31-4,016,312,30-5,124
19	32.32 ± 2.60	0.6668	51.222 ± 0.462	22-4,106,303,12-5,21-6,205,025
20	52.97 ± 3.88	0.7144	53.831 ± 0.504	31-5,32-1,32-2,116,007,130,40-1,40-2,320,13-1
21	78.25 ± 3.49	0.7412	55.257 ± 0.558	032,313,215,22-5,131,400,40-3,30-6,20-7,32-3,13-2,11-7,125,321
22	161.61 ± 6.54	0.7759	57.063 ± 0.537	304,017,41-1,41-2,132,033,12-6,401,40-4,224
23	186.58 ± 5.81	0.8010	58.346 ± 0.576	13-3,32-4,410,41-3,31-6,026,21-7,107,322,206,23-1,230
24	183.72 ± 6.34	0.8412	60.355 ± 0.673	NOT INDEXED

BACKGROUND = 432.16 ± 1.14

values of k_0, k_1, k_2 given above were found from the resultant curve by a least-squares analysis.

Also listed in Table 1 are the assigned indices hkℓ associated with the 2θ values b_n. The combination of the assigned indices hkℓ, the 2θ values b_n, and a least-squares program for a monoclinic unit cell enables the crystallographic parameters a, b, c, and β to be determined. In Table 2 these parameters are compared with those obtained at 77 °K by Chebotarev and Beznosikova (1959) and at room temperature by Zachariasen (1963). By using these lattice parameters a calculated 2θ position can be obtained for a given hkℓ. No calculated position for an assigned index hkℓ exceeds the 3σ range and 98.5% of the calculated positions do not exceed a 2σ range.

The lattice parameters given in Table 2 for α-Pu at 23 °K generate 16 indices whose calculated positions exceed the 3σ range of any observed Gaussian peak. These 16 indices are therefore classified as unobserved reflections. The 16 indices are 20-1, 200, 104, 21-3, 20-4, 120, 12-1, 022, 10-5, 212, 005, 121, 12-2, 223, 10-7, and 031.

At 23 °K the increases in the a and c lattice constants over the values observed at 77 °K correlate quite well with the observation of Lallement (1963). In a dilatometric investigation he found that a minimum in the thermal contraction of α-Pu occurs at approximately 50 °K. Below this temperature a polycrystalline sample of α-Pu begins to expand, and an explanation of this behavior is offered with the observed increase in the lattice parameters a and c.

Table 2. COMPARISON OF CRYSTALLOGRAPHIC CONSTANTS OF α-Pu AT 23 °K, 77 °K AND 294 °K.

	23 °K	77 °K	294 °K
a	6.143 ± 0.012, Å	6.118, Å	6.183 ± 0.001, Å
b	4.768 ± 0.011, Å	4.769, Å	4.822 ± 0.001, Å
c	10.987 ± 0.010, Å	10.940, Å	10.963 ± 0.001, Å
β	101.87 ± 0.17, deg	101.80, deg	101.79 ± 0.01, deg
Density	20.17, g/cc	20.32, g/cc	19.84, g/cc
Z	16	16	16
Space Group	$P2_1/m$	$P2_1/m$	$P2_1/m$

The structure of α-Pu at 23 °K is determined by a combination of the indices $hk\ell$, the observed values of I_n, and a least-squares program for the following equation:

$$I_n = k \sum_{1}^{j} M_j \, Lp_j \, (Fc_j)^2 \qquad (3)$$

where

$$Fc = 2.0 \sum_{1}^{8} \cos 2\pi(hx_i + \frac{k}{4} + lz_i)$$

The calculated structure factor, Fc, contains the positional parameters x_i and z_i of the plutonium atoms, which are summed over the eight atoms placed on a mirror plane, and multiplied by 2.0 (since there are two mirror planes in the unit cell) to account for the 16 atoms per unit cell. The structure factor is squared to obtain an intensity, multiplied by the Lorentz-polarization correction Lp_j, multiplied by the multiplicity factor M_j, and summed over j, the number of index triplets $hk\ell$ associated with each observed Gaussian peak. The quantity k is a scale factor.

In the least-squares analysis each I_n is weighted according to the reciprocal of its standard deviation squared. The unobserved reflections are also considered and according to Hamilton (1955) are assigned values of $I_{min}/3$ with estimated standard deviations of $\sigma = (4I_{min}^2/45)^{1/2}$. The value of I_{min} is taken as twice the standard deviation of the background. At this level we can be 95% confident that any intensity greater than this amount will have been observed. With Zachariasen's

room temperature structure of α-Pu as the initial starting point, the least-squares program processed the 23 observed I_n and the 16 unobserved reflections to yield values of x_i and z_i with their standard deviations. These values are listed in Table 3 along with Zachariasen's positional parameters for comparison. Examination of Table 3 indicates that there has been considerable movement in the atomic positions, but this observation is mitigated somewhat by the rather large standard deviations associated with the positions at 23 °K. A comparison between the observed and calculated I_n is given in Fig. 3. Also shown is the comparison between the unobserved reflections and their calculated counterparts.

DISCUSSION AND CONCLUSIONS

A convenient method for comparing crystal structures is to compare the polyhedral arrangement of atoms about a central atom under consideration. This is shown in Table 4 for α-Pu at 23 °K and 294 °K. In general, the number of neighboring atoms about a given atom is smaller at the lower temperature, which is indicative of a tendency for the atoms to cluster. The only exception to this generalization is for atom Pu(4) which picks up an additional atom as a neighbor at low temperature.

The interatomic distances in α-Pu at 23 °K and 294 °K are compared in Table 5. At room temperature, Zachariasen distinguishes between two types of bonds in α-Pu, "short" and "long." "Short" bonds range from 2.57 to 2.78 Å and "long" bonds range from 3.19 to 3.71 Å. An average bond length for all bonds is 3.19 Å.

Table 3. POSITIONAL PARAMETERS IN α-Pu AT 23 °K AND 294 °K

Atom	23 °K	294 °K
Pu(1)	x = 0.355 ± 0.020	0.345 ± 0.004
	z = 0.164 ± 0.013	0.162 ± 0.002
Pu(2)	= 0.749 ± 0.024	0.767 ± 0.004
	= 0.191 ± 0.015	0.168 ± 0.002
Pu(3)	= 0.032 ± 0.023	0.128 ± 0.004
	= 0.335 ± 0.010	0.340 ± 0.003
Pu(4)	= 0.578 ± 0.024	0.657 ± 0.005
	= 0.470 ± 0.013	0.457 ± 0.003
Pu(5)	= 0.091 ± 0.029	0.025 ± 0.005
	= 0.614 ± 0.014	0.618 ± 0.003
Pu(6)	= 0.390 ± 0.024	0.473 ± 0.004
	= 0.678 ± 0.014	0.653 ± 0.002
Pu(7)	= 0.367 ± 0.018	0.328 ± 0.004
	= 0.915 ± 0.015	0.926 ± 0.002
Pu(8)	= 0.911 ± 0.018	0.869 ± 0.004
	= 0.849 ± 0.013	0.894 ± 0.002

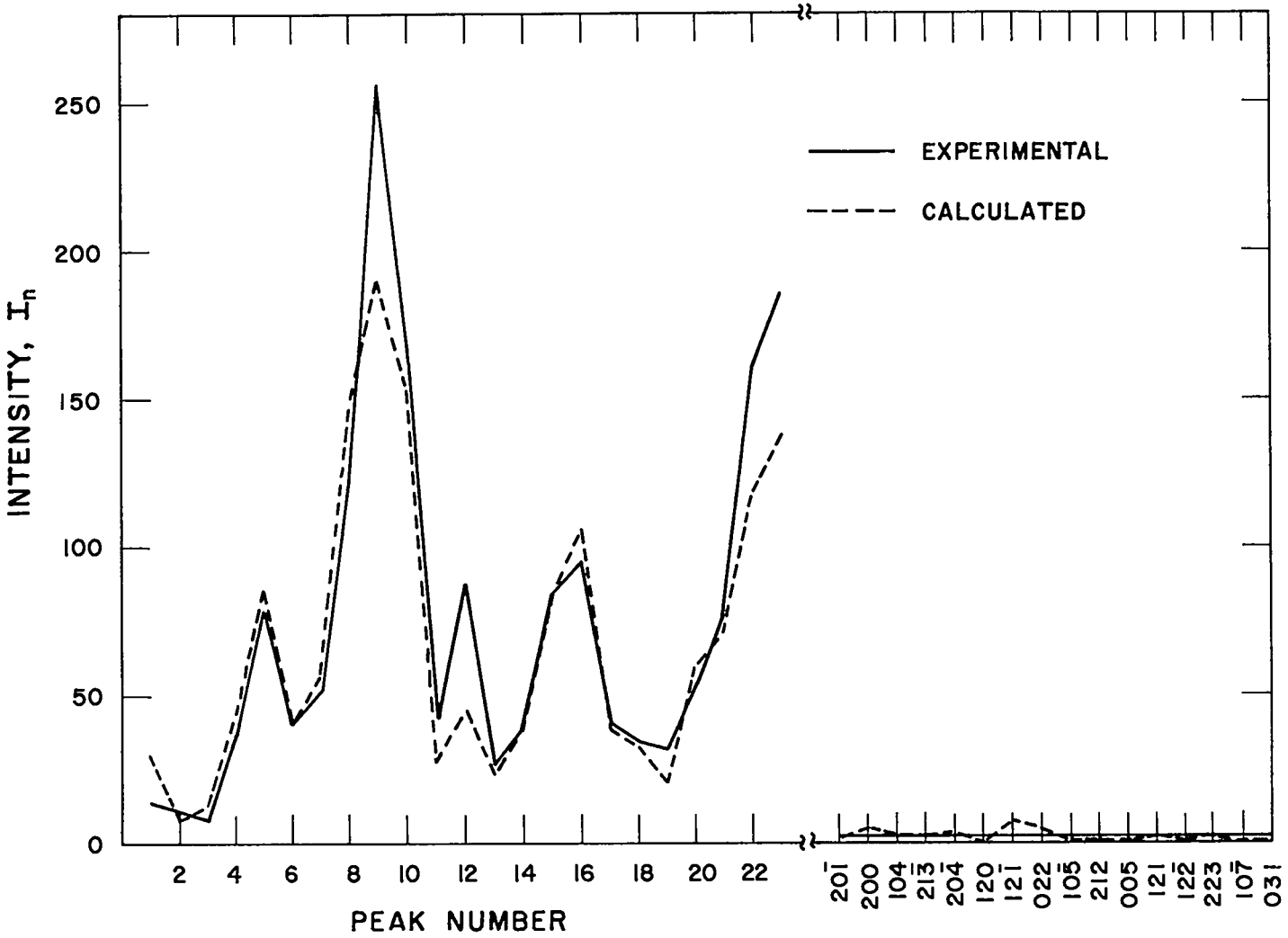

Fig. 3. Comparison between observed and calculated I_n for α-Pu at 23 °K. Also shown is the comparison between the unobserved reflections and their calculated counterparts.

Table 4. DESCRIPTION OF POLYHEDRA IN α-Pu

Atom	23 °K Neighboring Atoms	23 °K Polyhedron Description	294 °K Neighboring Atoms	294 °K Polyhedron Description
Pu(1)	10	16 three-sided faces	12	20 three-sided faces
Pu(2)	13	18 three-sided faces and 2 four-sided faces	14	24 three-sided faces
Pu(3)	13	22 three-sided faces	14	24 three-sided faces
Pu(4)	15	22 three-sided faces and 2 four-sided faces	14	24 three-sided faces
Pu(5)	12	20 three-sided faces	14	24 three-sided faces
Pu(6)	12	20 three-sided faces	14	24 three-sided faces
Pu(7)	11	14 three-sided faces and 2 four-sided faces	14	24 three-sided faces
Pu(8)	14	16 three-sided faces and 4 four-sided faces	16	28 three-sided faces

Table 5. INTERATOMIC DISTANCES IN α-Pu, Å

Atom	Neighbors	23 °K	Atom	Neighbors	294 °K
Pu(1)	Pu(2)	2.369 ± 0.346	Pu(1)	Pu(2)	2.597
	Pu(3)	3.007 ± 0.306		Pu(2)	3.588
	Pu(4)	3.364 ± 0.332		Pu(3)	2.584
	2Pu(6)	3.163 ± 0.339		Pu(4)	3.410
	Pu(7)	2.754 ± 0.322		2Pu(6)	3.203
	2Pu(7)	3.151 ± 0.322		Pu(7)	2.568
	2Pu(8)	2.879 ± 0.308		2Pu(7)	3.410
				2Pu(8)	2.758
				Pu(8)	3.170
Pu(2)	Pu(1)	2.369 ± 0.346	Pu(2)	Pu(1)	2.597
	Pu(3)	2.098 ± 0.345		Pu(1)	3.588
	Pu(4)	3.440 ± 0.368		Pu(3)	2.611
	2Pu(5)	3.221 ± 0.394		Pu(4)	3.374
	2Pu(6)	2.994 ± 0.374		2Pu(5)	3.426
	2Pu(7)	2.684 ± 0.359		2Pu(6)	3.613
	Pu(7)	3.434 ± 0.359		2Pu(7)	2.641
	2Pu(8)	3.261 ± 0.346		Pu(7)	3.386
	Pu(8)	4.087 ± 0.346		Pu(8)	3.193
				2Pu(8)	3.459

	Pu(3)	Pu(1)	3.007 ± 0.306	Pu(3)	Pu(1)	2.584
		Pu(2)	2.098 ± 0.345		Pu(2)	2.611
		Pu(4)	3.378 ± 0.331		Pu(4)	3.260
		Pu(4)	3.418 ± 0.331		2Pu(4)	3.365
		2Pu(4)	3.723 ± 0.331		Pu(4)	3.414
		2Pu(5)	2.598 ± 0.360		2Pu(5)	2.664
		Pu(5)	3.003 ± 0.360		Pu(5)	3.238
		2Pu(6)	4.303 ± 0.338		2Pu(6)	3.439
		2Pu(8)	3.192 ± 0.307		Pu(6)	3.652
					2Pu(8)	3.523
	Pu(4)	Pu(1)	3.364 ± 0.332	Pu(4)	Pu(1)	3.410
		Pu(2)	3.440 ± 0.368		Pu(2)	3.374
		Pu(3)	3.378 ± 0.331		Pu(3)	3.260
		Pu(3)	3.418 ± 0.331		2Pu(3)	3.365
		2Pu(3)	3.723 ± 0.331		Pu(3)	3.414
		2Pu(4)	2.697 ± 0.355		2Pu(4)	3.349
		Pu(5)	3.223 ± 0.382		Pu(5)	2.579
		2Pu(5)	3.380 ± 0.382		2Pu(5)	3.319
		Pu(6)	2.762 ± 0.361		Pu(6)	2.629
		2Pu(6)	2.921 ± 0.361		2Pu(6)	2.742
		Pu(8)	4.236 ± 0.333			

Table 5(continued)

Atom	Neighbors	23 °K	Atom	Neighbors	294 °K
Pu(5)	2Pu(2)	3.221 ± 0.394	Pu(5)	2Pu(2)	3.426
	2Pu(3)	2.598 ± 0.360		2Pu(3)	2.664
	Pu(3)	3.003 ± 0.360		Pu(3)	3.238
	Pu(4)	3.223 ± 0.382		Pu(4)	2.579
	2Pu(4)	3.380 ± 0.382		2Pu(4)	3.319
	2Pu(5)	3.468 ± 0.407		2Pu(5)	3.504
	Pu(6)	1.825 ± 0.388		Pu(6)	2.718
	Pu(8)	3.015 ± 0.361		Pu(6)	3.512
				Pu(7)	3.511
				Pu(8)	3.358
Pu(6)	2Pu(1)	3.163 ± 0.339	Pu(6)	2Pu(1)	3.203
	2Pu(2)	2.994 ± 0.374		2Pu(2)	3.613
	2Pu(3)	4.303 ± 0.338		2Pu(1)	3.439
	Pu(4)	2.762 ± 0.361		Pu(3)	3.652
	2Pu(4)	2.921 ± 0.361		Pu(4)	2.629
	Pu(5)	1.825 ± 0.388		2Pu(4)	2.742
	Pu(7)	2.629 ± 0.353		Pu(5)	2.718
	Pu(8)	3.356 ± 0.339		Pu(5)	3.512
				Pu(7)	3.295
				Pu(8)	3.214

Pu(7)	Pu(1)	2.754 ± 0.322	Pu(7)	Pu(1)	2.568
	2Pu(1)	3.151 ± 0.322		2Pu(1)	3.410
	2Pu(2)	2.684 ± 0.359		2Pu(2)	2.641
	Pu(2)	3.434 ± 0.359		Pu(2)	3.386
	Pu(6)	2.629 ± 0.353		Pu(5)	3.511
	2Pu(7)	3.256 ± 0.337		Pu(6)	3.295
	Pu(8)	2.747 ± 0.323		2Pu(7)	3.400
	Pu(8)	3.560 ± 0.323		Pu(8)	2.788
				Pu(8)	3.434
				2Pu(8)	3.489
Pu(8)	2Pu(1)	2.879 ± 0.308	Pu(8)	2Pu(1)	2.758
	2Pu(2)	3.261 ± 0.346		Pu(1)	3.710
	Pu(2)	4.087 ± 0.346		Pu(2)	3.193
	2Pu(3)	3.192 ± 0.307		2Pu(2)	3.459
	Pu(4)	4.236 ± 0.333		2Pu(3)	3.523
	Pu(5)	3.015 ± 0.361		Pu(5)	3.356
	Pu(6)	3.356 ± 0.339		Pu(6)	3.214
	Pu(7)	2.747 ± 0.323		Pu(7)	2.768
	Pu(7)	3.560 ± 0.323		Pu(7)	3.434
	2Pu(8)	4.054 ± 0.308		2Pu(7)	3.489
				2Pu(8)	3.507

A similar tendency to separate into "short" and "long" bonds is noted in α-Pu at low temperature. These bonds are listed in Table 6. Although the separation in range between "short" and "long" bonds is not as definite as in α-Pu at room temperature, there is nevertheless a rather clear-cut gap of approximately 0.2 Å separating the two regions.

Table 6. "SHORT" AND "LONG" BONDS IN α-Pu AT 23 °K, Å

Atom	Short Bonds		Long Bonds		All Bonds	
	No.	Range	No.	Range	No.	Mean Length
Pu(1)	5	2.37 - 3.01	5	3.15 - 3.36	10	2.99
Pu(2)	6	2.10 - 2.99	7	3.22 - 4.09	13	3.06
Pu(3)	5	2.10 - 3.01	8	3.19 - 4.30	13	3.27
Pu(4)	5	2.70 - 2.92	10	3.22 - 4.24	15	3.28
Pu(5)	5	1.83 - 3.02	7	3.22 - 3.47	12	3.03
Pu(6)	7	1.83 - 2.99	5	3.16 - 4.30	12	3.11
Pu(7)	5	2.63 - 2.75	6	3.15 - 3.56	11	3.03
Pu(8)	4	2.75 - 3.02	10	3.19 - 4.24	14	3.41

It should be noted that several apparently short interatomic bond distances appear in Tables 5 and 6. It is not believed that any Pu-Pu bond can ever approach these rather small values, but these are the results of the least-squares analysis. The standard deviations on the bond lengths are so large, however, that no significance whatsoever can be attached to these short distances.

At low temperature the upper limit of the "long" bond range and the lower limit of the "short" bond range have increased over their respective values at room temperature. The gross average Pu-Pu distance at low temperature is 3.16 Å, but this slight contraction in the distance of 3.19 Å at room temperature is not significant, because of the rather large standard deviations calculated for the interatomic distances.

In conclusion, α-Pu at 23 °K shows no gross crystallographic change from its structure at room temperature. The lattice constants, a and c, of the monoclinic unit cell are significantly larger than might be expected on the basis of extrapolated thermal contraction data but do correlate well with the minimum in thermal contraction as reported by Lallement (1963). The average number of interatomic neighbors is reduced to 12.5 at 23 °K compared with 14.0 at room temperature. A slight, but not significant, decrease in the average Pu-Pu distance was found, i.e., from 3.19 Å at room temperature to 3.16 Å at 23 °K.

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