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Interpretation of Monoclinic Powder X-ray Diffraction Patterns*

By W. H. Zachariasen

Department of Physics, University of Chicago, Consultant to Los Alamos Scientific Laboratory, U.S.A.

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The procedure used to index the monoclinic powder diffraction patterns of alpha and of beta plutonium metal is described.

This paper describes in some detail the procedure which was used to index the monoclinic powder X-ray diffraction patterns of alpha and of beta plutonium. The approach to the indexing problem is most simple and direct. No novel principles are involved, no computational aids are required, and only the most elementary knowledge of lattice geometry is needed. The practical use of the procedure will be illustrated with alpha plutonium as an example.

It is convenient to give the experimental data in the form of $\sin^2\theta_i$ (or $\sin^2\theta_i/\lambda^2$ or $4\sin^2\theta_i/\lambda^2$). Using the symbol $S_i \equiv \sin^2\theta_i$ one has for monoclinic symmetry:

$$S_i = H_i^2A_1 + K_i^2A_2 + L_i^2A_3 + 2H_iL_iA_{13} = T_i + K_i^2A_2 \quad (1)$$

where

$$A_1 = \lambda^2/4a_1^2\sin^2\beta,\ A_2 = \lambda^2/4a_2^2$$
$$A_3 = \lambda^2/4a_3^2\sin^2\beta,\ A_{13} = -\lambda^2\cos\beta/4a_1a_3\sin^2\beta\ . \quad (2)$$

Finding a_2

In any extensive set of data S_i will be many pairs S_i, S_j corresponding to reflections $(H_iK_iL_i)$ and $(H_iK_jL_i)$. For such pairs

$$S_i - S_j = (K_i^2 - K_j^2)A_2\ . \quad (3)$$

Accordingly one looks for recurrent values of differences $S_i - S_j$. For a primitive translation lattice the recurrent differences are $A_2, 3A_2, 4A_2, 5A_2, 7A_2 \ldots$ and for a centered translation lattice

$$(A, C, I)\ 4A_2, 8A_2, 12A_2, 16A_2, 20A_2 \ldots .$$

It is thus possible from inspection of differences $S_i - S_j$ to deduce the axis a_2 and to distinguish between a primitive and a centered translation lattice.

It is clearly true that the greater the accuracy of the experimental data the smaller is the probability of finding fortuitous recurrences in the set $S_i - S_j$.

Equation (3) does not hold for triclinic lattices. If recurrent differences are found, one can accordingly conclude that the symmetry is monoclinic rather than triclinic. (It is tacitly assumed that the possibility of symmetry higher than monoclinic was eliminated in advance.)

Example: α-Pu

Table 1 lists observed intensities and observed values $S_i = 10^5\sin^2\theta_i$ for the first 60 lines of the α-Pu pattern as obtained with a Norelco Diffractometer and Cu $K\alpha$ radiation. The maximum error in the S_i values is ±5.

Table 1. *X-ray diffraction data for alpha plutonium metal*

Line no.	Intensity	$S_i = 10^5 \times \sin^2\theta_i$	Line no.	Intensity	$S_i = 10^5 \times \sin^2\theta_i$	Line no.	Intensity	$S_i = 10^5 \times \sin^2\theta_i$
1	7	4637	21	42	11425	41	12	18169
2	7	6261	22	8	11737	42	70	18446
3	4	6482	23	25	12582	43	3	18758
4	27	6981	24		12628	44	6	18923
5	7	7043	25	10	13900	45	95	19079
6	56	7187	26		13961	46	31	20259
7	13	7377	27	37	14399	47	8	20547
8	122	7690	28	5	14583	48	17	21086
9	64	7737	29	5	15431	49	16	21558
10	105	8244	30	13	15633	50	10	21932
11	12	8804	31	16	15869	51	8	22563
12	152	8878	32	13	16208	52	11	22842
13	15	9032	33	16	16362	53	12	23091
14	11	9601	34	13	16518	54	4	24233
15	12	9922	35	19	16954	55	10	24405
16	246	10211	36	13	17125	56	36	24601
17	284	10290	37	6	16257	57	8	24940
18	121	10794	38	7	17594	58	6	25228
19	86	10924	39	17	17701	59	21	25630
20	15	11352	40	39	17948	60	11	25829

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Table 2. *Recurrent differences* $S_i - S_j$

i	j	$S_i - S_j$	i	j	$S_i - S_j$	i	j	$S_i - S_j$
6	1	2550	37	14	7656	16	0	10211
11	2	2543	38	15	7672	37	5	10214
13	3	2550	40	17	7658	38	7	10217
14	5	2558	42	18	7652	40	9	10211
15	7	2545	45	21	7654	42	10	10202
17	9	2553	49	25	7658	45	12	10201
18	10	2550	53	29	7660	49	20	10206
21	12	2547	56	35	7647	50	22	10195
25	20	2548				52	24	10214
34	26	2557				56	27	10202
35	27	2555				59	29	10199
36	28	2542				60	30	10196
41	30	2536						
43	32	2550						
44	33	2561						
46	39	2558						
53	47	2544						
59	53	2539						

When all possible differences $S_i - S_j$ are formed, one finds pronounced recurrences at 2550, 7657 and 10207 as shown in Table 2. Since these are in the ratio 1:3:4, a primitive monoclinic lattice with $A_2 = 2552$ and $a_2 = 4{\cdot}82$ Å is suggested.

Identifying potential *H0L* reflections

Determination of the unique axis a_2 in effect reduces the indexing problem from three to two dimensions. One should be in position to assign the correct index K_i to each diffraction line and to find the corresponding values $T_i = S_i - K_i^2 A_2$ which represent potential reflections from $(H0L)$ planes.

It must be remembered, however, that any experimental set S_i is incomplete. In the α-Pu case, for example, only 60 of the first 120 possible diffraction lines were actually observed. Hence one cannot expect to be able to deduce the values K_i and T_i for every diffraction line.

Any T_i-value that has been found implies the existence of other values $T_j = n^2 T_i$ corresponding to

Table 3. *Values* $T_i = S_i - K_i^2 A_2$

Line no.	S_i $K_i=0$		$S_i - A_2$ $K_i=1$		$S_i - 4A_3$ $K_i=2$	$S_i - 9A_2$ $K_i=3$	Line no.	S_i $K_i=0$		$S_i - A_2$ $K_i=1$		$S_i - 4A_2$ $K_i=2$		$S_i - 9A_3$ $K_i=3$
1	**4637**		2085				31	15869	or	13317	or	5663		
2	**6261**		3709				32	**16208**		13656		6002		
3	**6482**		3930				33	**16362**		13810		6156		
4	6981		**4429**				34	16518		**13966**		6312		
5	**7043**		4491				35	16954		**14402**		6748		
6	7187		**4635**				36	17125		**14573**		6919		
7	**7377**		4825				37	17257		14705		**7051**		
8	7690		**5138**				38	17594		15042		**7388**		
9	**7737**		5185				39	**17701**		15149		7495		
10	**8244**		5692				40	17948		15396		**7742**		
11	8804		**6252**				41	18169		**15617**		7963		
12	**8878**		6336				42	18446		15894		**8240**		
13	9032		**6480**				43	18758		**16206**		8552		
14	9601		**7049**				44	18923		**16371**		8717		
15	9922		**7370**				45	19079		16527		**8873**		
16	10211		7659		**5** ≈ 0		46	20259		**17707**		10051		
17	10290		**7738**		84		47	**20547**		17995		10341		
18	10794		**8242**		588		48	21086		**18534**		10880		
19	10924	or	8372	or	718		49	2158		19006		**11352**		
20	**11352**		8800		1146		50	21932		19380		**11726**		
21	11425		**8873**		1219		51	22563	or	20011	or	12357		
22	**11737**		9185		1531		52	22842		20290		**12636**		
23	12582	or	10030	or	2376		53	**23091**		**20539**		**12885**		128
24	**12628**		10076		2422		54	24233	or	21681	or	14027	or	1270
25	13900		**11348**		3694		55	24405	or	21853	or	14199	or	1442
26	**13961**		11409		3755		56	24601		22049		**14395**		1638
27	**14399**		11847		4193		57	24940	or	22388	or	14734	or	1977
28	**14583**		12031		4377		58	**25228**		22676		15022		2265
29	15431		**12879**		5225		59	25630		**23078**		15424		2667
30	**15633**		13081		5427		60	25829		23277		**15623**		2866

higher order reflections from the same ($H0L$) plane. If a given T_i-value corresponds to a reflection of order $m > 1$, then other possible values are

$$T_j = n^2 T_i / m^2 \qquad (4)$$

which should be sought out.

Example: α-Pu

In Table 3 are listed, for each datum S_i, all possible values $S_i - K_i^2 A_2$, with the selected T_i-values printed in bold-face type.

Recurrence is the obvious criterion for the selection of a T_i-value. For lines 4 and 8 the T_i-values are taken to be 4429 and 5138 because 4×4429 and 4×5138 are recurrent values $S_i - K_i^2 A_2$. Line 16 is assumed to represent the reflection (020) because $S_i \simeq 4A_2$. It is seen that the recurrent value $6480 = 4 \times 1620$ and $14578 = 9 \times 1620$, suggesting that 1620 is also a possible value T_i. Similarly $4635 = 9 \times 515$, $8242 = 16 \times 515$, $12882 = 25 \times 515$, $18534 = 36 \times 515$ and $25228 = 49 \times 515$, thus giving the additional T_i values of 515 and $2060 = 4 \times 515$ in accordance with equation (4).

With the limited data at hand it is not possible to decide for lines 19, 23, 31, 51, 54, 55 and 57 which is the correct choice of K_i and T_i. However, the analysis of the data of Table 3 has given 26 distinct T_i-values, and these are listed in ascending order in Table 4.

Table 4. *Deduced T_i-values*

No.	T_i
1	515
2	1620
3	2060 = 4 × 515
4	4427
5	4635 = 9 × 515
6	5137
7	6252
8	6480 = 4 × 1620
9	7049
10	7377
11	7738
12	8242 = 16 × 515
13	8878
14	11350
15	11737
16	12628
17	12879 = 25 × 515
18	13966
19	14399
20	14578 = 9 × 1620
21	15624
22	16207
23	16367
24	17704 = 4 × 4426
25	18534 = 36 × 515
26	20543 = 4 × 5136

Indexing the possible *H0L* reflections

The procedure described in the preceding section will have led to a set of quantities T_i corresponding to reciprocal lattice vectors ($H0L$), and it can be assumed in general that the set T_i so obtained is far from complete. (The T_i-values listed in Table 4 for the α-Pu example are for instance only two-thirds complete.)

Consider a set of four T_i-values corresponding to reciprocal lattice points with correct Miller indices as follows: ($H_1 0 L_1$), ($H_2 0 L_2$), ($H_2 - H_1$, 0, $L_2 - L_1$) and ($H_2 + H_1$, 0, $L_2 + L_1$). The T-values satisfy the condition.

$$2(T_{H_1 0 L_1} + T_{H_2 0 L_2}) = T_{H_2-H_1,0,L_2-L_1} + T_{H_2+H_1,0,L_2+L_1}\,. \quad (5)$$

Such a set will be called a tetrad and the quantity

$$\pm n = \begin{vmatrix} H_1 & L_1 \\ H_2 & L_2 \end{vmatrix}$$

will be referred to as the order of the tetrad.

It is always possible to choose a new set of axes in reciprocal space, $\mathbf{b}_1'$ and $\mathbf{b}_3'$, defined by

$$\begin{aligned} p\mathbf{b}_1' &= H_1\mathbf{b}_1 + L_1\mathbf{b}_3 \\ q\mathbf{b}_3' &= H_2\mathbf{b}_1 + L_2\mathbf{b}_3 \end{aligned} \qquad (6)$$

(where p and q are suitably chosen integers) by means of which all reciprocal lattice points can be generated. If

$$\begin{vmatrix} H_1 & L_1 \\ H_2 & L_2 \end{vmatrix} = \pm 1\,,$$

one can set $p = q = 1$, and the new vectors $\mathbf{b}_1'$, $\mathbf{b}_3'$ will form a primitive set. On the other hand, if

$$\left\| \begin{matrix} H_1 & L_1 \\ H_2 & L_2 \end{matrix} \right\| > 1\,,$$

either p or q or both > 1, and the resulting vector set $\mathbf{b}_1'$, $\mathbf{b}_3'$ may not be primitive.

Any set of four experimental T-values (as deduced by the process described in the preceding section) satisfying the condition

$$2(T_i + T_j) = T_k + T_l \qquad (7)$$

is a possible tetrad. If the set forms a true tetrad (*i.e.* if equation (7) is not satisfied merely by chance), one can (in accordance with equation (5)) index the four corresponding reciprocal lattice points as ($p00$), ($00q$), ($p0\bar{q}$), ($p0q$), and in the process cell dimensions a_1', a_3', β' are determined.

The practical procedure is first to set $p = q = 1$.

Table 5. *Possible tetrads*: $2(T_i + T_j) = T_k + T_l$

No.	i	j	$2(T_i+T_j)$	k	l	T_k+T_l	a_1	a_3	β	N/n
I	2	5	12510	6	10	12514	6·18 Å	3·66 Å	101·8°	16/3
II	3	4	12974	2	14	12970	9·08	6·18	143·7	8
III	2	6	13514	5	13	13513	6·51	3·65	111·6	16/3
IV	1	7	13534	8	9	13529	10·78	3·08	94·6	8
V	1	8	13990	7	11	13990	10·96	3·09	101·7	8
VI	1	9	15128	7	13	15130	11·41	3·09	110·2	8
VII	1	10	15784	4	14	15777	23·30	6·18	152·6	16
VIII	1	11	16506	6	14	16487	17·20	4·43	141·3	11·5
IX	3	7	16624	11	13	16610	5·39	3·08	94·6	4

Table 6. *Indexing of T_i-values for the various tetrads*

		Tetrads									
No.	T_i	I *H0L*	II *H0L*	III *H0L*	IV *H0L*	V *H0L*	VI *H0L*	VII *H0L*	VIII *H0L*	IX *H0L*	Correct *H0L*
1	515				(100)	(100)	(100)	(100)	(100)		001
2	1620	(100)	($10\bar{1}$)	(100)				$30\bar{1}$			100
3	2060		(100)		200	200	200	200	200	(100)	002
4	4427		(001)					($10\bar{1}$)			102
5	4635	(001)		($10\bar{1}$)	300	300	300	300	300		003
6	5137	($10\bar{1}$)		(001)				$60\bar{1}$	($10\bar{1}$)		$10\bar{3}$
7	6252				(001)	($10\bar{1}$)	($10\bar{1}$)	$70\bar{2}$		(001)	$20\bar{1}$
8	6480	200	$20\bar{2}$	200	($10\bar{1}$)	(001)	$20\bar{1}$	$60\bar{2}$			200
9	7049		$30\bar{2}$		(101)	$20\bar{1}$	(001)	$80\bar{2}$			$20\bar{2}$
10	7377	(101)		$20\bar{1}$				(001)			103
11	7738				$20\bar{1}$	(101)	$30\bar{1}$	$50\bar{2}$	(001)	($10\bar{1}$)	201
12	8242		200		400	400	400	400	400	200	004
13	8878	$20\bar{1}$		(101)	201	$30\bar{1}$	(101)	$90\bar{2}$		(101)	$20\bar{3}$
14	11350		(101)					(101)	(101)		104
15	11737		$40\bar{2}$		301	$40\bar{1}$	201	$10,0,\bar{2}$			$20\bar{4}$
16	12628							$80\bar{1}$			$10\bar{5}$
17	12879				500	500	500	500	500		005
18	13966							$10,0,\bar{3}$			$30\bar{1}$
19	14399							$11,0,\bar{3}$			$30\bar{2}$
20	14578	300		300				$90\bar{3}$			300
21	15624				401	$50\bar{1}$	301	$11,0,\bar{2}$		201	$20\bar{5}$
22	16207							$80\bar{3}$			301
23	16367							201			105
24	17704		002		$50\bar{1}$	401	$60\bar{1}$	$20\bar{2}$			204
25	18534	002	300		600	600	600	600	600	300	006
26	20543		$50\bar{2}$	002	501	$60\bar{1}$	401	$12,0,\bar{2}$	$20\bar{2}$		$20\bar{6}$

If the selected tetrad is a true one and of order 1, the trial cell so obtained will be capable of explaining all observed data.

In general the chosen tetrad will be of order $|n| > 1$, and the trial cell corresponding to $p = q = 1$ will then be able to explain only $1/n$ of the observed T_i-values. Accordingly one must try out the various combinations $p = 1, 2, 3, \ldots, q = 1, 2, 3, \ldots$ until one finds a set of small integers p, q which makes possible the indexing of all reflections.

The cell arrived at by the procedure just described may not be primitive, and in general it will not correspond to a conventional choice of axes. However, the reduction to a primitive set $\mathbf{a}_1, \mathbf{a}_3$ chosen in accordance with conventions is a trivial task.

If the density is known, the content of any trial cell obtained with $p = q = 1$ can be computed. For any true tetrad the trial cell must contain N/n molecules, where N is the number of molecules in the correct cell.

It is obvious that an extensive set of experimental T-values will yield many tetrads, and that any one of them (which is not fortuitous) can be used for the indexing.

α-Pu

The list of T_i-values deduced for α-Pu is given in Table 4. In searching for tetrads it should be remembered that each datum of Table 4 is precise to ± 5 or better. Accordingly a possible tetrad will be regarded as acceptable only if the two sides of equation (7) differ by less than 20.

The data of Table 4 lead to a great many possible tetrads. The nine corresponding to the smallest values of $T_k + T_l$ are listed in Table 5 together with the

Table 7. *Correct indices for the first sixty diffraction lines*

Line no.	S_i	*HKL*	Line no.	S_i	*HKL*
1	4637	003, 012	31	15869	$30\bar{3}$, 213
2	6261	$20\bar{1}$	32	16208	301
3	6482	200	33	16362	105
4	6981	112	34	16518	$31\bar{1}$
5	7043	$20\bar{2}$	35	16954	$31\bar{2}$
6	7187	013	36	17125	310
7	7377	103	37	17257	$22\bar{2}$
8	7690	$11\bar{3}$	38	17594	123
9	7737	201	39	17701	204
10	8244	004	40	17948	221, $10\bar{6}$
11	8804	$21\bar{1}$	41	18169	$21\bar{5}$
12	8878	$20\bar{3}$	42	18446	024
13	9032	210	43	18758	311
14	9601	$21\bar{2}$	44	18923	115
15	9922	113	45	19079	$22\bar{3}$
16	10211	020	46	20259	214
17	10290	211	47	20547	$20\bar{6}$
18	10794	014	48	21086	016
19	10924	$11\bar{4}$	49	21558	124
20	11352	104	50	21932	$22\bar{4}$
21	11425	$21\bar{3}$	51	22563	303
22	11737	$20\bar{4}$	52	22842	$12\bar{5}$
23	12582	212	53	23091	025, 205, $21\bar{6}$
24	12628	$10\bar{5}$	54	24233	$32\bar{1}$, $10\bar{7}$
25	13900	114	55	24405	$31\bar{5}$
26	13961	$30\bar{1}$	56	24601	$32\bar{2}$
27	14399	$30\bar{2}$	57	24940	116
28	14583	300	58	25228	007
29	15431	015	59	25630	215
30	15633	$20\bar{5}$	60	25829	$22\bar{5}$

dimensions of the trial cells for $p=q=1$ and the cell content calculated from the experimental density of 19·8 g.cm^{-3}.

Table 6 shows the observed T_i-values which can be indexed for each of the nine tetrads. It is seen that tetrad no. VII can explain every observed T_i-value (and, indeed, with the previously found axis a_2, all S_i-values of Table 1).

The indexing problem is thus solved, with the cell

$$a_1'=23{\cdot}30,\ a_2=4{\cdot}82,\ a_3'=6{\cdot}18\ \text{Å},\ \beta'=152{\cdot}6^\circ.$$

However, the choice of axes is unconventional. It is customary to select the two shortest lattice vectors in the XZ plane as the vectors $\mathbf{a}_1$ and $\mathbf{a}_3$. Accordingly one chooses new axes defined by $\mathbf{a}_1=\mathbf{a}_3'$, $\mathbf{a}_3=\mathbf{a}_1'+3\mathbf{a}_3'$ giving

$$a_1=6{\cdot}18,\ a_2=4{\cdot}82,\ a_3=10{\cdot}96\ \text{Å},\ \beta=101{\cdot}8^\circ.$$

The corresponding transformations for Miller indices are: $H=L'$, $L=H'+3L'$.

The last column of Table 6 gives the indices of the T_i-values referred to the conventional cell. The correct index assignment for the first sixty lines of the diffraction pattern is shown in Table 7.

Only one (VIII) of the possible tetrads given in Table 5 is incorrect, corresponding to chance fulfilment of the tetrad relation of equation (7). The other tetrads of Table 5 are of order $|n|>1$, so that one has to choose $pq>1$. The p and q values required for complete indexing are as follows:

Tetrad no.	p	q
I	1	3
II	2	1
III	3	3
IV	2	2
V	1	2
VI	1	2
IX	4	4

The cells obtained with these p and q values are primitive for tetrads I, II, V, VI, doubly primitive for tetrads IV and IX and triply primitive for tetrad III. However, in all instances the correct cell is obtained by simple axis transformation.

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Die Kristallstruktur des Tetramethylammonium-Disilberjodids*

Von Hans-Jürgen Meyer

Mineralogisch-Petrologisches Institut der Universität Bonn/Rhein, Deutschland

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The compound $N(CH_3)_4Ag_2I_3$ belongs to the space group *Pnam* (D_{2h}^{16}) and has the lattice parameters $a=17{\cdot}7_7$, $b=10{\cdot}07_1$, $c=7{\cdot}43_7$ Å; $Z=4$ molecules. The structure contains tetrahedrally coordinated double chains $[Ag_4I_6]^{2-}_{\infty}$ parallel to [001], similar to those in $CsAg_2I_3$ and $CsCu_2Cl_3$. The $N(CH_3)_4^+$ complexes are surrounded by 12 I atoms.

1. Darstellung und makroskopische Eigenschaften

Tetramethylammonium–Disilberjodid, $N(CH_3)_4Ag_2J_3$, gehört zu einer Klasse von Komplexsalzen mit organischen Kationen, die in neuerer Zeit von Kuhn & Schretzmann (1955, 1957; vgl. auch Datta & Ghosh, 1914) durch Reaktionen in Dimethylformamid erhalten wurden. Eine Probe dieser Substanz wurde freundlicherweise durch Herrn Prof. Kuhn zur Verfügung gestellt. Eine grössere Substanzmenge wurde als Ausgangsprodukt für Kristallisationsversuche auf folgende Weise gewonnen: Vereinigt man eine heisse, gesättigte Lösung von AgJ in konz. Jodwasserstoffsäure mit einer konz. wässrigen Lösung von $N(CH_3)_4J$, so fällt $N(CH_3)_4Ag_2J_3$ in reichlichen Mengen aus. Durch Umkristallisieren aus Dimethylformamid (Hinweis von R. Kuhn) erhält man die Verbindung in völlig farblosen Nadeln des orthorhombischen Systems von meist 0,1–0,2 mm Dicke und wenigen mm Länge. Die morphologisch vorherrschende Kombination ⟨100⟩ + ⟨110⟩ bedingt einen pseudohexagonalen Habitus. Mikroskopisch waren an den Nadelenden noch ⟨021⟩ und weitere Formen erkennbar. Es besteht gute Spaltbarkeit nach (100). Die Kristalle sind recht spröde und zeigen plattig-splittrigen bis muschligen Bruch. Das fein gemörserte Pulver ist etwas lichtempfindlich (bräunlich-rosa Verfärbung). Die Dichte wurde nach der Schwebemethode (in $CH_2J_2+CHJ_3$) zu $d \gtrsim 3{,}34$ bestimmt.

Der optische Charakter ist positiv-zweiachsig in der Nadelrichtung, die Brechungsindices sind (für Na_D und 20 °C)

$$\alpha=1{,}757;\ \beta=1{,}770;\ \gamma=1{,}912\ (\pm 0{,}002);$$

daraus errechnet sich der Achsenwinkel $2V_\gamma=37^\circ$. Orientierung: $\alpha \parallel [010]$, $\beta \parallel [100]$, $\gamma \parallel [001]$.

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