~~SECRET~~
~~SECURITY INFORMATION~~
Date 7/27/53 Initials D.L.T.

This Document Consists of 7 Pages
This is Copy 143 of 157A

MLM-808

Category - PHYSICS AND MATHEMATICS

UNCLASSIFIED

W0-36166

A REDETERMINATION OF THE LATTICE
PARAMETERS OF POLONIUM

BY

J. M. GOODE

Classification cancelled (or changed to)

by authority of

by

TISOR, date

UNCLASSIFIED

~~RESTRICTED DATA~~

~~This document contains restricted data
as defined by the Energy Act of
1946. The contents of this document
and unauthorized person is prohibited.~~

This document is
PUBLICLY RELEASABLE

High Commissioner

Authorizing Official

Date

Date: January 30, 1953

~~SECRET~~

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

~~SECRET~~

UNCLASSIFIED

MLM-808

Category - PHYSICS AND MATHEMATICS

STANDARD DISTRIBUTION

Mound Laboratory	1 through 28
AF Plant Representative, Burbank	29
AF Plant Representative, Seattle	30
AF Plant Representative, Wood-Ridge	31
ANP Project Office, Fort Worth	32
Argonne National Laboratory	33 through 40
Armed Forces Special Weapons Project (Sandia)	41
Armed Forces Special Weapons Project, Washington	42
Army Chemical Center	43
Atomic Energy Commission, Washington	44 through 46
Battelle Memorial Institute	47
Bechtel Company	48
Brookhaven National Laboratory	49 through 51
Bureau of Ships	52
California Research and Development Company	53 through 54
Carbide and Carbon Chemicals Company (C-31 Plant)	55 through 56
Carbide and Carbon Chemicals Company (K-25 Plant)	57 through 58
Carbide and Carbon Chemicals Company (ORNL)	59 through 64
Carbide and Carbon Chemicals Company (Y-12 Plant)	65 through 68
Chicago Patent Group	69
Chief of Naval Research	70
Columbia University (Havens)	71
Commonwealth Edison Company	72
Department of the Navy - Op-362	73
Detroit Edison Company	74
Directorate of Research (WADC)	75
duPont Company, Augusta	76 through 78
Foster Wheeler Company	79
General Electric Company (ANPP)	80 through 82
General Electric Company, Richland	83 through 86
Goodyear Atomic Corporation	87 through 88
Hanford Operations Office	89
Idaho Operations Office	90 through 93
Iowa State College	94
Kirtland Air Force Base	95
Knolls Atomic Power Laboratory	96 through 99
Los Alamos Scientific Laboratory	100 through 101
Massachusetts Institute of Technology (Kaufmann)	102
Monsanto Chemical Company	103
National Advisory Committee for Aeronautics, Cleveland	104
National Bureau of Standards	105
Naval Medical Research Institute	106
Naval Research Laboratory	107 through 108
New Brunswick Laboratory	109
New York Operations Office	110 through 111
North American Aviation, Inc.	112 through 114
Nuclear Development Associates, Inc.	115
Patent Branch, Washington	116
Pioneer Services & Engineering Company	117
Pratt & Whitney Aircraft Div.	118
RAND Corporation	119
Sandia Corporation	120
Savannah River Operations Office, Augusta	121
USAF Headquarters	122
U. S. Naval Radiological Defense Laboratory	123
UCLA Medical Research Laboratory (Warren)	124
University of California Radiation Laboratory, Berkeley	125 through 129
University of California Radiation Laboratory, Livermore	130 through 132
University of Rochester	133 through 134
Vitro Corporation of America	135 through 136
Walter Kidde Nuclear Laboratories, Inc.	137
Westinghouse Electric Corporation	138 through 141
Yale University	142
Technical Information Service, Oak Ridge	143 through 157

~~SECRET~~

UNCLASSIFIED

MLM-808

INTERNAL DISTRIBUTION

1. Carroll A. Hochwalt
2. N. N. T. Samaras
3. J. J. Burbage
4. R. A. Staniforth
5. E. C. McCarthy
6. J. F. Eichelberger
7. E. A. Rembold
8. D. L. Scott
9. D. L. Timma
10. J. E. Bersuder
11. J. W. Heyd
12. E. S. Spoerl
13. R. J. Cote
14. G. A. Essig
15. G. Pish
16. J. M. Goode
17. W. H. Waldo
18. K. Kasschau, Office Res. and Med., Oak Ridge
19. F. R. Dowling, Office Prod. and Eng., Oak Ridge
20. J. H. Roberson, Area Manager, AEC, Dayton, Ohio
21. Central Files
22. Central Files
23. Central Files
24. Central Files
25. Central Files
26. Central Files
27. Central Files
28. Central Files

Issued:

AUG 7 1953

ABSTRACT

A more precise determination of the lattice parameters and X-ray density of polonium has been made with the use of the extrapolation method of Bradley and Jay. The low-temperature simple cubic phase has a lattice parameter of $a_0 = 3.359 \pm 0.002\text{\AA}$ and an X-ray density of 9.196 ± 0.006 gram per cubic centimeter at 39°C . The high-temperature rhombohedral phase has lattice parameters of $a_0 = 3.366 \pm 0.002\text{\AA}$, $\alpha = 98^\circ 5' \pm 2'$, and an X-ray density of 9.398 ± 0.006 gram per cubic centimeter at 39°C .

INTRODUCTION

The crystal structure of polonium was first studied by M. A. Rollier, S. B. Hendricks, and L. R. Maxwell¹ by means of electron diffraction. They interpreted the structure as monoclinic with $a_0 = 7.42\text{\AA}$, $b_0 = 4.29\text{\AA}$, $c_0 = 14.10\text{\AA}$, and $\alpha = 90^\circ$.

Later work was done by Maxwell and Beamer² at Los Alamos in 1946. Their results indicated that polonium exists in two phases a low-temperature simple cubic phase with $a_0 = 3.345\text{\AA}$ and a high-temperature simple rhombohedral phase with $a_0 = 3.359\text{\AA}$ and $\alpha = 98^\circ 13'$.

Diffraction studies of polonium carried out at Mound Laboratory have indicated that the lattice parameters obtained by Maxwell and Beamer are slightly in error. More correctly, the low-temperature phase has a lattice parameter of $a_0 = 3.359 \pm 0.002\text{\AA}$ and the high-temperature phase has lattice parameters of $a_0 = 3.366 \pm 0.002\text{\AA}$ and $\alpha = 98^\circ 5' \pm 2'$ at 39°C .

METHODS AND RESULTS

The X-ray samples used to refine the values of the polonium lattice parameters were prepared by a method similar to that used by Maxwell and Beamer.² The polonium was purified by fractional volatilization in an evacuated fused-silica tube. The polonium was then volatilized into a thin-walled, fused-silica X-ray capillary. Only patterns taken soon after preparation could be considered because of the rapid conversion of polonium to lead.

The data for the high-temperature or beta-polonium phase were taken from a total of five patterns obtained from three samples. The data for the low-temperature or alpha-polonium phase were taken from a total of four patterns from two samples. The history of these patterns is given in Table I.

TABLE I
PATTERN HISTORY

SAMPLE	PATTERN	POLONIUM DECAYED (%)	POLONIUM PHASE	INTERNAL STANDARD
51	51 1	$\frac{1}{2}$	β	NONE
59	59 1	$1\frac{1}{2}$	β	Ta
59	59 2	4	β	Ta
68	68 1	$\frac{1}{2}$	β	Au
68	68 2	1	β	Au
51	51 2	1	α	NONE
51	51 2	$1\frac{1}{2}$	α	NONE
59	59 1	$1\frac{1}{2}$	α	Ta
59	59 2	4	α	Ta

The patterns were taken with a General Electric powder camera with a nominal diameter of 143 millimeters. Straumanis technique³ was used for correcting for radius and film-shrinkage errors.

The values of the lattice parameters were obtained by extrapolating to $\cos^2 \theta = 0$ by the method of Bradley and Jay.⁴ The beta polonium was treated as a hexagonal structure, and the results were converted to the rhombohedral structure after all other calculations were made.

The beta-polonium structure was indexed by two methods. The first method followed that of Maxwell and Beamer.² They pointed out that for $\alpha = 98^\circ 13'$ for the rhombohedral structure several sets of possible powder lines are in coincidence. This occurs for an axial ratio of $c = \sqrt{15/16}$ in the hexagonal indexing. The lattice parameters were calculated for the hexagonal and rhombohedral structures with the use of this axial ratio. The axial ratio was also calculated so as to give the best possible fit of the individual lines to the average value of a_0 . The lattice parameters for the hexagonal and rhombohedral structures were calculated with the use of this axial ratio.

The patterns were then rechecked for splitting of some of the lines that would be prohibited by an axial ratio of $c = \sqrt{15/16}$. Pattern No. 68-2, which had sharp but spotty lines, showed four cases of splitting of these lines. The split was approximately equal in magnitude to the separation of lines observed due to the difference in wavelength of K_{α_1} and K_{α_2} radiation.

The extrapolated values for the lattice parameter, a_0 , for the hexagonal and cubic cases are given in Table II.

TABLE II
POLONIUM LATTICE PARAMETERS

PATTERN NO	INDEXING	AXIAL RATIO, c	INTERPLANAR SPACING, a_0 ($\text{\AA}$)	STATISTICAL PROBABLE ERROR OF AVERAGE, a_0 ($\text{\AA}$)
51-1	HEXAGONAL	$\sqrt{15/16}$	5.0906	± 0.0022
59-1	HEXAGONAL	$\sqrt{15/16}$	5.0880	± 0.0025
59-2	HEXAGONAL	$\sqrt{15/16}$	5.0870	± 0.0020
68-1	HEXAGONAL	$\sqrt{15/16}$	5.0902	± 0.0025
68-2	HEXAGONAL	$\sqrt{15/16}$	5.0886	± 0.0011
AVERAGE	HEXAGONAL	$\sqrt{15/16}$	5.0889	DENSITY = 9.406 g/cc
AVERAGE	RHOMBOHEDRAL	$\alpha = 98^\circ 13'$	3.3660	
51-1	HEXAGONAL	0.9723	5.0839	± 0.0005
59-1	HEXAGONAL	0.9723	5.0840	± 0.0017
59-2	HEXAGONAL	0.9723	5.0836	± 0.0010
68-1	HEXAGONAL	0.9723	5.0844	± 0.0005
68-2	HEXAGONAL	0.9723	5.0836	± 0.0003
AVERAGE	HEXAGONAL	0.9723	5.0839	DENSITY = 9.398 g/cc
AVERAGE	RHOMBOHEDRAL	$\alpha = 98^\circ 5'$	3.3660	
51-2	SIMPLE CUBIC		3.3593	± 0.0005
51-3	SIMPLE CUBIC		3.3595	± 0.0003
59-1	SIMPLE CUBIC		3.3592	± 0.0004
59-2	SIMPLE CUBIC		3.3595	± 0.0004
AVERAGE	SIMPLE CUBIC		3.3594	DENSITY = 9.196 g/cc

By virtue of the better fit and the fact that splitting of some lines which are in coincidence for $c = \sqrt{15/16}$ was observed, the axial ratio of 0.9723 was accepted as the more probable value. This gave, for the hexagonal case, lattice parameters (interplanar spacing and interaxial angles) of $a_0 = 5.0839\text{\AA}$, $c_0 = 4.9431\text{\AA}$, and for the rhombohedral case, $a_0 = 3.3660\text{\AA}$, $\alpha = 98^\circ 5'$. Since there was no question of indexing the patterns of alpha polonium, the lattice parameter could be obtained directly. This value was $a_0 = 3.3594\text{\AA}$.

The X-ray density was computed by calculating the volume of the unit cell from the observed lattice parameters and by calculating the mass inside that volume from the known number of polonium atoms inside the unit cell.

DISCUSSION

Systematic errors were minimized or reduced by use of the extrapolation method of Bradley and Jay, which eliminated errors due to sample absorption and eccentricity. The use of cameras equipped for the Straumanis technique eliminated errors due to uniform film shrinkage and uncertainty in camera-radius.

There were, however, random errors which were not eliminated. Variations of the sample temperature would cause a broadening of the diffraction lines (strains and lattice imperfections also cause broadening) and reduce the accuracy of measurement of these lines. The accuracy of measurement was such that the fourth decimal place was affected even in the back-reflection region. Nonuniform film shrinkage introduced another random error which may have affected the fourth decimal place.

The random error was estimated by calculation of the probable error of the mean value of a_0 . This was 0.0002 $\text{\AA}$ for both the rhombohedral and the cubic cases. As the systematic errors were included in the data for these calculations, the probable error was actually somewhat smaller than 0.0002 $\text{\AA}$. The error in a_0 due to random errors was set at 0.001 $\text{\AA}$. This assured (on a statistical basis) that the true a_0 had a 99 per cent chance of falling within that error.

The temperature of the sample could not be determined because of the internal heating of the polonium. Previous work⁵ has shown that the temperature of the phase change is 36°C and that the two phases may coexist between 18° and 54°C . Since both phases were present in the patterns used for this study, the temperature of the sample was between room temperature (24°C) and 54°C . Setting the sample temperature at 39°C allowed 15°C uncertainty in the temperature of the sample. Previous work⁶ on the coefficient of expansion has shown that for the alpha phase α is 24×10^{-6} centimeter per centimeter per degree from -196° to 30°C . If this figure is used for both phases, a temperature uncertainty of 15°C would lead to an uncertainty of approximately 0.001 $\text{\AA}$ in the lattice parameters.

The total uncertainty in the lattice parameters is the sum of that due to random errors and that due to temperature uncertainty. The total uncertainty is, then, 0.002 $\text{\AA}$.

CONCLUSIONS

On the basis of the discussion, the computed values for the lattice parameters and densities of polonium are

Simple Cubic Indexing - α -polonium

$$a_0 = 3.359 \pm 0.002\text{A at } 39^\circ\text{C}$$

$$\rho = 9.196 \pm 0.006 \text{ g/cc}$$

Rhombohedral Indexing - β -polonium

$$a_0 = 3.366 \pm 0.002\text{A at } 39^\circ\text{C}$$

$$\alpha = 98^\circ 5' \pm 2'$$

Hexagonal Indexing - β -polonium

$$a_0 = 5.084 \pm 0.003\text{A at } 39^\circ\text{C}$$

$$c_0 = 4.943 \pm 0.003\text{A}$$

$$\rho = 9.398 \pm 0.006 \text{ g/cc}$$

REFERENCES

1. Rollier, M. A., Hendricks, S. B., and Maxwell, L. R., J. Chem. Phys., 4, 648 (1936).
2. Beamer, W. H. and Maxwell, C. R., J. Chem. Phys. 17, 1293 (1949).
3. Straumanis, M. and Ievins, A., Naturwiss, 23, 833 (1935).
4. Bradley, A. J. and Jay, A. H., Proc. Phys. Soc. (London) 44, 563 (1932).
5. Goode, J. M., The Temperature of the Phase Transitions of Polonium, MLM-615, October 1, 1951.
6. Goode, J. M., Rpt. Gen. Res., MLM-484-1, p 1-55, September 11, 1950.