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Citation: The Journal of Chemical Physics **4**, 648 (1936); doi: 10.1063/1.1749762
View online: http://dx.doi.org/10.1063/1.1749762
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/4/10?ver=pdfcov
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through water vapor or else in the gases pumped out of the discharge. We are not concerned with the discharge proper in which reactions may be caused by ions as discussed in detail by Brewer.[17]

Again we assume H and OH as primary products, since O is produced at a comparatively small concentration. The main result of the present paper is that the disappearance of OH is largely due to a termolecular gas reaction. From our failure to observe the absorption spectrum of H_2O_2 and from the results of Campbell and Rodebush and of Geib, $H+OH+M \rightarrow H_2O+M$ is to be assumed as the most plausible process. A wall reaction is certain not to play a predominant part for a clean glass surface but to become important at the KCl surface.

In addition it is possible that H_2O_2 is produced but rapidly decomposed so that no appreciable concentration builds up, since H atoms and OH radicals are both able to decompose it.[18]

[17] A. K. Brewer, J. Phys. Chem. **38**, 1051 (1934).

[18] Cf. K. H. Geib, Zeits. f. physik. Chemie **A169**, 161 (1934). Evidence for the decomposition process $OH+H_2O_2$ will be presented in another paper.

OCTOBER, 1936 JOURNAL OF CHEMICAL PHYSICS VOLUME 4

The Crystal Structure of Polonium by Electron Diffraction

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(Received July 2, 1936)

Electron diffraction photographs ($\lambda=0.062$A) were obtained from about 10^{-7} g of polonium that had been volatilized in a stream of hydrogen and condensed over an area of about 3 mm² on a thin collodion film. Diffraction patterns were also obtained from bismuth and tellurium since it was expected that polonium would have a similar crystal structure. Analysis of these patterns shows that the structure of polonium closely resembles that of tellurium, the lattice being pseudohexagonal with $a=4.25$A, $c=7.06$A, or 14.12A, and the calculated density 9.39 assuming 3 Po in the pseudo unit of structure. The true lattice is probably monoclinic with $a=7.42$A, $b=4.29$A, $c=14.10$A and β quite close to 90°, a suggested value being $\beta=92°$; the calculated density for 12 Po in the unit of structure is 9.24. A structure, based upon the space group C_2^3-C2, in which each polonium atom has four nearest neighbors gives moderate agreement between observed and calculated intensities of reflection.

INTRODUCTION

POLONIUM is the superior homolog of tellurium in the periodic system of the elements and immediately follows bismuth in atomic number. It resembles both these elements in its chemical properties but, of course, differs from them in being radioactive. The crystal structure of the element could be expected to be similar to that of tellurium or bismuth.

Sufficiently large amounts of polonium have not yet been available for x-ray diffraction experiments and thus no information is available on its crystal structure or its density. A strong source of polonium for radioactive work contains *ca.* 10^{-6} g of material, which is quite sufficient to give electron diffraction photographs provided that it can be obtained as a thin film.

PREPARATION OF THE POLONIUM FILM

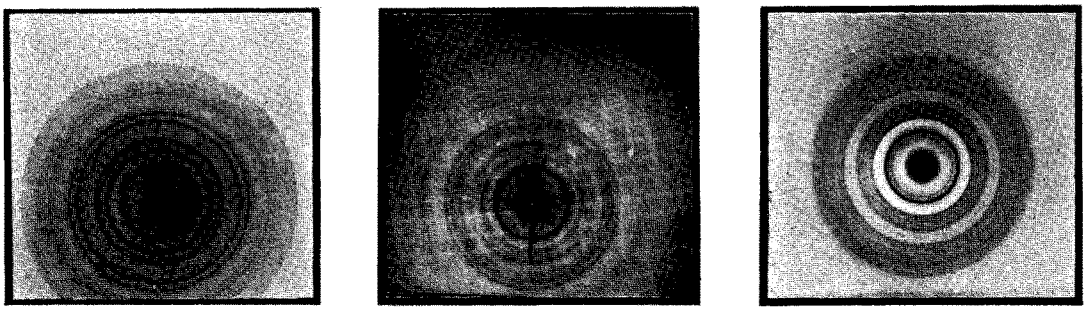
Pure polonium was prepared from old radon bulbs[1] under the supervision and with the constant help of Dr. L. R. Hafstad[2] who has developed a technique for the production of strong polonium sources after the method used by Mme. I. Curie.[3] According to this method

* On leave of absence from the University of Milan. I am particularly indebted to Professor Dr. G. Bruni, Dr. Charles L. Parsons, Dr. H. G. Knight and Dr. C. H. Kunsman for making arrangements necessary for the successful culmination of this work and for their many courtesies.

[1] We are indebted to Dr. C. F. Burnham and Dr. F. West of the Kelly Hospital, Baltimore, Maryland, for the liberal supply of old radon bulbs that they placed at our disposal. The purification of the polonium was carried out at the National Bureau of Standards. Successful completion of the work was due in a large part to the cooperation of Dr. Hafstad, of the Department of Terrestrial Magnetism, Carnegie Institution of Washington.

[2] L. R. Hafstad, J. Frank. Inst. **221**, 191 (1936).

[3] I. Curie, J. chim. phys. **22**, 471 (1925).



Bismuth
λ = 0.062A
plate dist. = 24.5 cm.

Polonium
λ = 0.0622A
plate dist. = 24.5 cm.

Tellurium
λ = 0.059A
plate dist. = 24.3 cm.

FIG. 1. Electron diffraction photographs of bismuth, polonium and tellurium (full size).

the polonium is separated from the solution containing salts of radium D and E by displacement on silver, complete separation is shown by absence of β-ray activity. The polonium was finally displaced from solution upon a cleaned and outgassed nickel disk. A film was obtained by evaporating the polonium from the nickel base in a stream of pure hydrogen and condensing the vapor on a very thin collodion film supported by a fine platinum gauze. The volatilizing apparatus used was similar to that described by Rona and Schmidt,[4] and Curie and Joliot.[5] During the evaporation process the nickel was maintained at a dull red heat which was sufficient to volatilize the polonium[6] without carrying over traces of nickel. A dark visible coating was obtained over an area of about 3 mm^2 on the collodion film.

Electron diffraction photographs were taken immediately after preparation of the sample since the radioactivity of the polonium soon destroyed the film. α-ray air ionization measurements taken after the film was destroyed showed the presence of about 1500 e.s.u. or 2.52×10^{-7} g of polonium remaining on the wire support. It is estimated that the original thickness of the polonium film was not less than 100A.

Electron Diffraction Apparatus

The apparatus used for electron diffraction has been described elsewhere.[7] Electrons with a de Broglie wave-length of about 0.06A were used with a film to plate distance of 245.6 mm. Preliminary tests were made with collodion films upon which lead, bismuth and tellurium had been volatilized in the apparatus mentioned above. The lead films were prepared from about 10^{-6} g of the element that had been deposited upon nickel. In all these cases the diffraction photographs obtained were in complete agreement with the crystal structure data for these elements. There was only slight evidence of scattering from collodion on any of the photographs.

Five electron diffraction photographs were obtained from polonium films at de Broglie wave-lengths between 0.0623 and 0.0627A. One of these is reproduced in Fig. 1 together with photographs from bismuth and tellurium. Average values of $Q=1/d^2=4\sin^2\theta/\lambda^2$ as measured on the polonium photographs are listed in Table I together with the estimated intensities of reflection.

The Lattice and Crystal Structure of Polonium

Diffraction rings of polonium can roughly be accounted for, as shown in Table I, on the basis of a hexagonal lattice having $a=4.254$A and $c=7.06$A. These lattice dimensions are the expected ones if the structure of polonium is similar to that of tellurium or bismuth. Moreover, as shown in Table II, the intensities are not greatly unlike those of tellurium. However, closer inspection shows that neither the above lattice nor the one having $c=14.12$A can be correct. It perhaps can be seen on the electron diffraction photograph of polonium reproduced

[4] E. Rona and E. A. W. Schmidt, Zeits. f. Physik **48**, 784 (1928).
[5] I. Curie and F. Joliot, J. chim. phys. **28**, 201 (1931).
[6] P. Bonét-Maury, Ann. de physique **11**, 253 (1929).
[7] S. B. Hendricks, L. R. Maxwell, V. L. Mosley and M. E. Jefferson, J. Chem. Phys. **1**, 549 (1933).

TABLE I. *Electron diffraction data from polonium interpreted according to a hexagonal lattice.*

Ring No.	Q Obs.	Q Calc.	Pseudo hexagonal indices	Intensity* (obs.)
1	0.0890 to 0.0940	0.0919	(10.1)	*vs*
2	0.1580	0.1520	(10.2)	*m*
3	0.1804	0.1805	(00.3)	*ms*
4	0.2175	0.2210	(11.0)	*w*
5	0.2481	0.2415	(11.1)	*mw*
6	0.2642	0.2522	(10.3)	*w*
7	0.3634	0.3730	(20.2)	*w*
8	0.370			*vw*
9	0.4068	0.3925	(10.4)	*m*
		0.4016	(11.3)	
10	0.4480			*m*
11	0.46	0.4732	(20.3)	*vw*
12	0.5310	0.5340	(21.1)	*s*
		0.5418	(11.4)	
13	0.7170	0.7216	(00.6)	*w*
		0.7221	(11.5)	
14	0.8000	0.7940	(20.5)	*vw*
15	0.8465	0.8436	(30.3)	*w*
16	0.8953	0.8840	(22.0)	*w*
		0.9040	(22.1)	
17	0.9920	0.9640	(22.2)	*mw*
		1.014	(20.6)	
18	1.149	1.136	(31.3)	*vw*
		1.177	(40.0)	
19	1.248	1.257	(40.2)	*vw*
20	1.473	1.456	(31.5)	*w*
		1.478	(32.2)	
		1.498	(40.4)	
21	1.627	1.624	(00.9)	*vw*
		1.627	(41.2)	

* The following abbreviations are used throughout this work; *vs*, very strong; *s*, strong; *ms*, medium strong; *m*, medium; *mw*, medium weak; *w*, weak; *vw*, very weak.

in Fig. 1 that the first ring is quite broad, as is also true for some of the other rings. The (8) and (10)–(11) rings cannot be accounted for by the hexagonal lattice and the agreement between observed and calculated values of $Q=4\sin^2\theta/\lambda^2$ is extremely poor for the (2), (7) and (10)–(11) rings. This lack of agreement is not changed by doubling the value of c.

Before continuing the direct structure argument for polonium it is best to point out some of the structural characteristics of the elements in the 5th and 6th subgroups of the periodic system; the pertinent facts are summarized in Table III. Both the bismuth and tellurium type structures can be considered as distortions of the mercury structure which is itself a deformation of a close-packed structure. Each mercury atom has six nearest neighbors; in bismuth the displacement is 0.15A along the c axis, leading to three nearest neighbors, and in tellurium 0.25A perpendicular to that axis such as to give two nearest neighbors. As the atomic number increases in either series the differences in distance between nearest and next nearest neighbors decreases. Now if the pseudo lattice of polonium is approximately correct and if the pseudo parameter values are those of tellurium then the distances to surrounding atoms are those shown in Table III.

The true lattice of polonium is probably a monoclinic one and it is logical to suppose that the space group is the monoclinic subgroup common to both $D_3^4-C3_12$ and $D_{3d}^5-R\bar{3}m$, namely C_2^3-C2. A strictly analogous situation is found for plaster of Paris, $2\,CaSO_4\cdot H_2O$, which as studied by x-ray powder diffraction methods[8] was found to have a structure based on the enantiomorphic space groups $D_3^4-C3_12$ and $D_3^6-C3_22$. Earlier and more thorough work on single crystals of $2\,CaSO_4\cdot H_2O$,[9] however, shows that the true lattice is monoclinic with $\beta=90°\ 38'$

TABLE II. *Diffraction results from tellurium.*

Q Obs.	Q Calc.*	Indices	Intensity* X-ray	Electron	Polonium
0.097	0.0966	(10.1)	*s*	*s*	*vs*
.184	.1840	(10.2)	*ms*	*ms*	*m*
.201	.2024	(11.0)	*m*	*m*	*w*
.231	.2315	(11.1)	*w*	*mw*	*mw*
.263	.2620	(00.3)	*w*	*w*	*ms*
.302	.2990	(20.1)	*m*	*m*	
.322	.3190	(11.2)	*vw*	*vw*	
	.3295	(10.3)			*w*
.396	.3860	(20.2)	*m*	*w*	*w*
.469	.4645	(11.3)	*m*	*m*	*m*
	.4722	(21.0)			
.496	.5013	(21.1)	*w*	*w*	*s*
.533	.5332	(10.4)	*w*	*w*	*m*
	.5318	(20.3)			

* The formula used was $Q=0.06746(h^2+k^2+hk)+0.02911l^2$ corresponding to a lattice having $a=4\,445$ and $c=5.86$A, the value of c being slightly smaller than 5.91A as found by Bradley (Phil. Mag. **48**, 477(1924)) from x-ray diffraction.

TABLE III. *Structures of some elements of the 5th and 6th subgroups of the periodic table.*

Element	Space Group	Hexagonal Lattice Dimensions A: a	c	c/a	Neighboring Atoms: No.	Distance	No.	Distance
As	$D_{3d}^5-R\bar{3}m$	3 76	10 57	2.81	3	2.51	3	3.15
Sb	$D_{3d}^5-R\bar{3}m$	4.26	11.29	2.65	3	2.87	3	3.37
Bi	$D_{3d}^5-R\bar{3}m$	4 56	11.85	2.60	3	3 10	3	3 47
Se	$D_3^4-C3_12$	4 33	9.94	2.28	2	2 32	4	3 46
Te	$D_3^4-C3_12$	4.44	11.82	2.66	2	2 86	4	3.74
Pseudo polonium lattice		4.25	14.12	3.32	—	3.10	—	3.58

[8] W. A. Caspari, Nature **133**, 648 (1934).
[9] P. Gallitelli, Periodico di Mineralogia **4**, 132 (1933).

TABLE IV. *Electron diffraction data from polonium with suggested monoclinic indices.*

Ring No.	Observed Q	Intensity	Pseudo hexagonal indices	Q Calc.	Monoclinic indices	Q Calc.	Calculated values of $J \cdot S/F_{Po}^2$
1	0.0890	*vs*	(10.1)	0.0919	$(20\bar{2})$	0.0900	230
	−0.0940				$(11\bar{2})$	0.0911	10
					(112)	0.0927	460
					(202)	0.0950	10
2	0.1580	*m*	(10.2)	0.1520	$(20\bar{4})$	0.1471	20
					$(11\bar{4})$	0.1497	380
					(114)	0.1551	20
					(204)	0.1577	240
3	0.1804	*ms*	(00.3)	0.1805	(006)	0.1800	300
4	0.2175	*w*	(11.0)	0.2210	(020)	0.2176	70
					(310)	0.2173	250
			(11.1)	0.2415	$(31\bar{2})$	0.2336	80
					(022)	0.2376	40
5	0.2481	*mw*			(312)	0.2414	20
			(10.3)	0.2522	$(20\bar{6})$	0.2444	60
					$(11\bar{6})$	0.2484	80
6	0.2642	*w*			$(11\bar{6})$	0.2564	40
					(206)	0.2604	4
			(20.1)	0.3129	$(40\bar{2})$	0.3043	0
					$(22\bar{2})$	0.3070	100
					(222)	0.3123	10
					$(40\bar{2})$	0.3149	100
7	0.3634	*w*	(20.2)	0.3730	$(40\bar{4})$	0.3590	60
					$(22\bar{4})$	0.3642	100
8	0.370	*vw*			(224)	0.3750	300
					(404)	0.3802	10
			(11.3)	0.4016	$(31\bar{6})$	0.3853	100
9	0.4068	*m*			$(02\bar{6})$	0.3973	150
					$(31\bar{6})$	0.4093	460
			(10.4)	0.3925	$(20\bar{8})$	0.4030	50
					$(11\bar{8})$	0.3977	440
					$(11\bar{8})$	0.3870	40
					$(20\bar{8})$	0.3818	80
10	0.4480	*m*	(20.3)	0.4732	$(40\bar{6})$	0.4536	100
					$(22\bar{6})$	0.4616	90
11	0.46	*vw*			$(22\bar{6})$	0.4776	60
					$(40\bar{6})$	0.4856	10
12	0.5310	*s*	(21.1)	0.5340	$(51\bar{2})$	0.5202	70
					$(42\bar{2})$	0.5217	40
					$(13\bar{2})$	0.5256	50
					(132)	0.5282	170
					(422)	0.5321	140
					$(51\bar{2})$	0.5336	200
			(11.4)	0.5418	$(31\bar{8})$	0.5213	80
					$(02\bar{8})$	0.5373	110
					(318)	0.5533	100

and $a/b=1.744$ instead of 1.732 and that the space group is probably C_2^3-C2. This conclusion has recently been challenged[10] but the properties of the crystal, particularly the biaxial character, gives it strong support.

The quadratic form for a monoclinic lattice is:

$$Q=\frac{4\sin^2\theta}{\lambda^2}=\frac{h^2}{a^2\sin^2\beta}+\frac{k^2}{b^2}+\frac{l^2}{c^2\sin^2\beta}-\frac{2\cos\beta}{ac\sin^2\beta}hl.$$

Now if the lattice is pseudohexagonal about the c axis β must be near 90° and thus $\sin\beta$ must be approximately unity while $\cos\beta$ is very sensitive to deviations from 90°. The pseudohexagonal (00.3) becomes the monoclinic (006) and thus $c\sin\beta$ is 14.10A and c is very close to 14.10A. If the structure is pseudohexagonal the intensities of the reflections from the monoclinic $(hk0)$ should differ chiefly by the multiplicity factor. Thus both (020)(310)←(11.0) should have an appreciable intensity. If the limits of Q for the fourth line are taken as 0.2175 ± 0.035 then $b=4.29\pm0.04$A and $a=7.42\pm0.07$, giving $a/b=1.763$ to 1.700 and

$$Q=0.0181h^2+0.0544k^2+0.0050l^2-0.0190\cos\beta hl.$$

In estimating the value of β it is noted that (1)

[10] W. A. Caspari, Proc. Roy. Soc. **A155**, 41 (1936). Note that the Laue photograph as reproduced *does not* have a threefold axis.

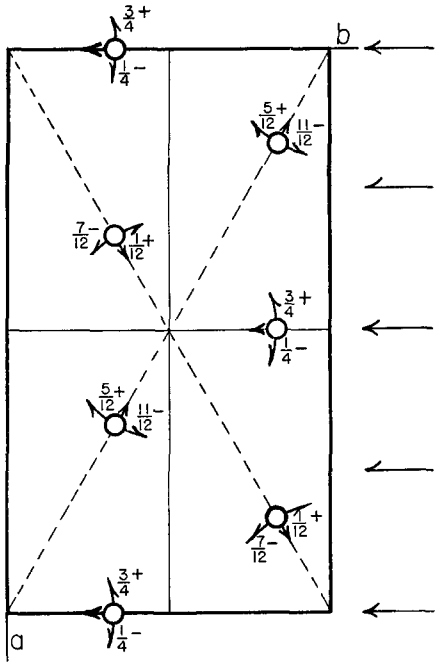


FIG. 2. A projection showing the relationship of the polonium structure to that of bismuth and tellurium as obtained by deformation from the mercury structure. The full arrows that are parallel to the *ab* plane represent deformation towards tellurium and the curved half arrows toward polonium. Bismuth positions are obtained by displacements along the normal to the *ab* plane.

is broad, that (2) does not agree well with the pseudohexagonal spacing, and that the agreement between observed and the calculated value of (10) for the pseudo lattice is poor (Table I). A suggested value of $\cos\beta$ is -0.035 which corresponds to $\beta=92°$. Values of Q calculated on the basis of this lattice for planes possibly contributing to the first twelve lines of the polonium diffraction pattern are listed in Table IV. The agreement between observed and calculated values of Q is quite satisfactory.

If the space group is $C_2{}^3-C2$ the polonium atoms are probably in three sets of general positions: xyz; $\bar{x}y\bar{z}$; $\frac{1}{2}+x$, $\frac{1}{2}+y$, z; $\frac{1}{2}-x$, $\frac{1}{2}+y$, $\bar{z}$.[11] Parameters corresponding to the hexagonal tellurium positions are

$$\begin{array}{lll} x_1=0.00, & x_2=\ 0.14, & x_3=0.36, \\ y_1=\ .27, & y_2=-.14, & y_3=\ .36, \\ z_1=\ .25, & z_2=\ \ .42, & z_3=\ .08. \end{array}$$

The intensity of the pseudohexagonal (10.3) which is present on the polonium photograph but absent for tellurium cannot be explained by use of these values, nor by considerable distortion of them with the symmetry of $C3_12$ tending to equalize the distances of nearest and next nearest neighbors.

Inspection of Table I further shows that the pseudohexagonal planes corresponding to the (13)–(21) lines either are $3n$ orders of $(00.l)$ or usually have low values of l. The probable explanation for the latter fact is that the spacings of the monoclinic planes derived from a particular pseudohexagonal plane are grouped quite close together for low values of l. This is well illustrated by the strong (12) ring as shown in Table IV, there being eight possible contributing monoclinic forms. The high intensity of the (3) ring and the possible presence of reflections from (0012) and (0018) strongly suggests that the c parameters of polonium are quite close to those of tellurium.

After considerable work it was found that the following parameter values gave moderate agreement between observed and calculated intensities of reflection as perhaps can be seen by inspection of Table IV, column 8.

$$\begin{array}{lll} x_1=0.05, & x_2=\ 0.13, & x_3=0.35, \\ y_1=\ .27, & y_2=-.20, & y_3=\ .40, \\ z_1=\ .245, & z_2=\ \ .43, & z_3=\ .07. \end{array}$$

It is not considered that these particular parameter values are the correct ones but a deformation of this type from the tellurium structure is probably required by the data. They lead to the following approximate separations of the polonium atoms:

$x_1y_1z_1$ to $x_2y_2z_2$, 3.50A, 3.34A and 4.06A;
$x_1y_1z_1$ to $x_3y_3z_3$, 3.30A, 3.38A and 3.95A.

This distortion is in such a direction as to give four nearest neighbors at a distance of about 3.40A about a particular polonium atom.

A projection of the above structure on (001) is shown in Fig. 2 together with the indicated relationship to a similar projection of the bismuth and tellurium positions.

The density calculated, for the atomic weight 210, on the basis of the monoclinic lattice is 9.24 and for the pseudohexagonal lattice 9.39. The calculated atomic volume is 22.7 cc per mole, a value to be expected from a consideration of the atomic volume-atomic number relationships of the elements of high atomic weight.

[11] *Int. Tables for the Determination of Crystal Structures*, (Berlin, 1935), Vol. I.