THE CRYSTAL STRUCTURE OF METALLIC TELLURIUM AND SELENIUM AND OF STRONTIUM AND BARIUM SELENIDE*

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Abstract

X-ray spectrograms were made using the powder method of Hull, with monochromatic MoKα rays. Both tellurium and selenium are found to crystallize in simple triangular lattices with axial ratios 1.33 and 1.14, respectively, and with sides of unit basal triangle equal to 4.44 A and 4.34 A, respectively. In each case three atoms are grouped at each corner. The densities computed from these measurements are 6.25 and 4.84, respectively. Strontium selenide and barium selenide both have a simple cubic structure, with cube edges equal to 3.117$\pm$.003 A and 3.308$\pm$.005 A respectively. In the case of SrSe the ions at the corners are Sr^{++} and Se^{--}, and the calculated density is 4.53.

X-RAY photographs were taken by the well-known powder method described by A. W. Hull.[1] A narrow beam of monochromatic rays is passed through the powdered material and produces a pattern of lines on a film bent on an arc of a circle, at whose center the powdered material is placed. These lines are due to the reflection of the rays from the planes in the small crystals, one line for each kind of plane. From the position and intensity of the lines the crystal structure can be found.

In all of the following work the powdered sample was mixed with about five volumes of wheat flour to decrease absorption and was loaded into a glass capillary tube. The rays used were the molybdenum α doublet, obtained by filtration through zirconium.

Tellurium

Metallic tellurium is listed by Groth[2] as trigonal, isomorphous with metallic selenium.

Two photographs were taken, giving identical patterns. The observations are tabulated in Table I. The intensities were obtained by assigning to the strongest line a value of ten, and estimating the others on this basis. Using the graphs described by Hull and Davey,[3] a match was found on the single triangular lattice, at axial ratio 1.33. The values in column

* The results in this paper have been presented before American Physical Society; see Abstracts in Phys. Rev. **21**, pp. 22 and 378 (1923).

[1] A. W. Hull, Phys. Rev. **10**, 661, (1917); **17**, 571 (1921).

[2] Groth, Chemische Krystallographie, vol. 1, p. 34.

[3] Hull and Davey, Phys. Rev. **17**, 549 (1921).

3 were calculated for the plane spacings of a simple triangular lattice with axial ratio of 1.33 and with the side of unit basal triangle equal to 4.44 A.

TABLE I

Tellurium

Planes	Spacing of planes observed	calculated	Estimated intensity
10.0	3.83 A	3.832 A	2
10.1, 00.1(2)	3.22	3.224	10
10.2	2.34	2.340	5
11.0	2.22	2.220	4
11.1	2.08	2.078	2
00.1(3), 10.0(2)	1.969	1.967	2
20.1	1.834	1.834	4
11.2	1.777	1.776	2
10.1(2)	1.614	1.614	2.5
12.0, 11.3, 00.1(4)	1.469	1.471	3
12.1	1.412	1.411	2
20.3, 10.4	1.377	1.378	2
12.2	1.307	1.304	1
30.1	1.267	1.256	0.3
00.1(5), 10.2(2) and 12.3, 30.2	1.171	1.171	3
10.5	1.130	1.129	0.8

The density determined from the dimensions of the unit prism comes out 2.083, taking the number of atoms associated with each unit prism as one-half. The specific gravity given by Groth is 6.233 and 6.388. This would mean that at each point of the lattice there are three atoms of tellurium, making the density from crystallographic data equal to 6.225. This has recently been confirmed by A. J. Bradley[4] who gives $a = 4.835$A, the atoms being located on Schoncke's point systems, No. 23 or 24, i.e., a right-handed or left-handed spiral around the trigonal axes. The metals bismuth[5] and antimony[6] have been found to have a similar structure but with two atoms associated with each point.

SELENIUM

Groth gives very little data for metallic selenium, except that it is hexagonal, isomorphous with metallic tellurium.

Two photographs were obtained, each giving the same pattern. Data are tabulated in Table II. A match was found on the simple triangular graph. Values for the third column are calculated for the simple triangular lattice, with an axial ratio $c = 1.14$ and with the side of unit basal triangle equal to 4.34 A.

[4] A. J. Bradley, Phil. Mag. (6) **48**, No. 285 (Sept. 1924)
[5] R. W. James, Phil. Mag. **42**, 193 (1921)
[6] Norman Tunstall and R. W. James, Phil. Mag. **40**, 233 (1920)

The density comes out 1.613 assuming one half atom per unit prism. Since the accepted specific gravity of selenium is 4.47 to 4.6, the calculations would indicate that, as in the case of tellurium, three atoms of selenium are associated with each point of the lattice. Bradley[4] has also confirmed this. The density from crystallographic data, therefore, is 4.84.

TABLE II

Planes	Spacing of planes observed	Spacing of planes calculated	Estimated intensity
10.0	3.77 A	3.773 A	8
10.1, 00.1(2)	3.01	3.013	10
11.0	2.17	2.170	2
10.2	2.07	2.069	2.5
11.1	1.997	1.999	2
10.0(2)	1.880	1.879	0.2
20.1	1.770	1.768	1.7
11.2, 00.1(3)	1.638	1.637	1.5
10.3, 10.1(2)	1.505	1.506	1.5
12.0	1.425	1.422	1.5
11.3	1.310	1.310	0.3
10.4	1.175	1.178	0.3
11.4	1.075	1.075	0.2

COMPOUNDS OF SELENIUM

From a study[7] of the compounds of the halides with the alkali metals, using CsI and RbBr as starting points, values for the ionic radii of the monovalent elements have been found. This method might be extended to the determination of the sizes of the divalent ions, provided measurements of BaTe, SrTe, BaSe, and SrSe could be made.

Strontium selenide, a white powder which becomes reddish brown on exposure to air, was made by heating $SrSeO_3$ to a dull red heat in a stream of hydrogen. For calibration purposes, NaCl was photographed on each film with the substance analyzed.

TABLE III

Strontium selenide (No. 494)

NaCl (read)	SrSe (read)	SrSe (corrected)	Log *d*	Planes
2.85 A	3.19 A			
2.020	2.24			
1.640	1.882	1.801	.49407	111
1.419	1.574	1.561	.49443	100(2)
1.269	1.408	1.397	.49468	210
1.158	1.281	1.271	.49312	211
1.002	1.110	1.102	.49372	110
.942	1.046	1.039	.49374	221, 100(3)
.893	.991	.985	.49344	310
	.945	.940	.49382	311
	.836	.835	.49482	321

[7] W. P. Davey, Phys. Rev. **22,** 211-220 (Sept. 1923)

Two photographs were taken, measurements being made directly in angstrom units on a scale described by W. P. Davey.[8] Results for one are given in Table III.

From the planes which appear the structure is seen to be simple cubic. The mean value of logarithm of *d*, the side of the unit cube, found by use of probability paper is .49400, hence *d* is 3.119 A. The density, calculated from the dimensions of the unit cube and its weight, comes out 4.512. The other photograph gave $d = 3.116$ A, and density $= 4.544$.

A rough measurement by the displacement method for powders gave the value 4.18. The errors in the displacement method are such as to tend to make the value for the density come out too low. The agreement is, however, sufficiently close to give a check on the interpretation of the diffraction pattern.

The unit crystal of SrSe is then a simple cube of ions, with Sr^{++} and Se^{--} occupying alternate corners of a cube whose side is $3.117 \pm .003$ A.

Barium selenide was made by reducing $BaSeO_3$ with hydrogen at a red heat. Two photographs were taken. Results from one are given in Table IV.

TABLE IV

Barium selenide (No. 457)

NaCl (read)	BaSe (read)	BaSe (corrected)	Log 2*d*	Planes
2.81	3.80 A	3.80 A		
1.987	3.30	3.30		
1.621	2.33	2.33		
1.404	1.990	1.994	.82042	311
1.256	1.901	1.905	.81948	111(2)
1.148	1.648	1.652	.82007	100(2)
.994	1.475	1.478	.82108	210(2)
.936	1.348	1.351	.82076	211(2)
.888	1.167	1.169	.82038	110(3)
	1.099	1.101	.81884	100(2) and 221
	1.042	1.044	.81973	310(2)
	.995	.997	.82042	311(2)
	.882	.884	.82054	321

The structure is seen to be simple cubic. The mean logarithm of 2*d* from probability curve is .82025; *d* then is equal to 3.305 A. The value in the fourth column is 2*d* because the logarithm which is added to the logarithm of the values of corrected measurements of BaSe has been taken for planes of higher order than the first. The second photograph gave $d \pm 3.310$ A.

Density measurements were not made because of the small amount of the sample available. Barium selenide has then a simple cubic structure of ions, with length of side of cube equal to $3.308 \pm .005$ A.

[8] W. P. Davey, J. Opt. Soc. Amer. R.S.I. **5**, (Nov. 1921)

Barium and strontium tellurides. Several attempts have been made to obtain photographs of these compounds. They were made in several different ways, including heating together in hydrogen the oxides of the metals and TeO_2 and heating a mixture of carbon and tellurate in hydrogen, with only moderate success. In every case the x-ray analysis gave photographs of metallic tellurium with additional lines which were too few and too faint to be of any use. The probability is that the telluride was decomposed after it was made, by the moisture of the air to which it was exposed while being packed into the tiny tube. There was certainly telluride present in all of the samples before they were photographed.

VASSAR COLLEGE,
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