The Crystal Structure of β Selenium

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The crystal structure of β selenium as reported by Burbank (1952) is shown to be in error. From reanalysis of intensity data of the type $hk0$ the Se_8 molecule is shown to be a puckered ring rather than a chain. This ring has approximate symmetry $\bar{8}2m$, as in α selenium. Satisfactory packing between Se_8 molecules is also obtained with the revised parameters, and there appears to be very little structural difference between α selenium and β selenium.

Evidence is presented that a single crystal of β selenium may transform into an aggregate of crystals of hexagonal selenium rather than into a single crystal as proposed by Burbank.

Introduction

There has recently been reported by Burbank (1952) a determination of the crystal structure of β selenium. The determination was made by an apparently rather straightforward use of the Harker–Kasper inequalities on the $h0l$ data, coupled with a Fourier non-negativity technique applied to the $hk0$ data by means of X-RAC; $0kl$ data were used for refinement of parameters. The unit of structure is monoclinic, with $a_0 = 12\cdot85$, $b_0 = 8\cdot07$, $c_0 = 9\cdot31$ Å, $β = 93° 8'$, and space group $P2_1/a$. Parameters are given for the 32 selenium atoms (four molecules), which lie in general positions in the unit cell.

The author points out that the results are at striking variance with those for α selenium, in which the molecules were found to be eight-membered rings, with average bond distance 2·34 Å and average bond angle 105·3° (Burbank, 1951). The reported parameters for β selenium correspond to an eight-atom chain molecule, the distance between atoms 8 and 1, 3·04 Å, being so great as not to correspond to a bond between these atoms (see Fig. 1). The author concluded that 'to a first approximation the β molecule is an eight-membered chain formed by breaking one bond in a ring molecule and leaving one terminal atom double-bonded to its neighbor while the other terminal atom is single-bonded to its neighbor'. A structure of this sort could conceivably result from the transfer of an electron from atom 2 to atom 8.

However, the close similarity in color of the two monoclinic forms of selenium strongly suggests that the same eight-membered rings are present in both of them. Moreover, the separation of charge and the replacement of two single bonds by one double bond would be expected to lead to great instability of β selenium. Another surprising feature of the reported

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structure is the existence of interatomic packing distances between Se_8 molecules of 2·85 and 2·86 Å, whereas the shortest distance in α selenium is 3·53 Å. These abnormal features suggest that the reported structure for β selenium is erroneous.

The final parameters were determined by Burbank largely by use of the two-dimensional Fourier projections along the a and b axes. These projections showed uniformity of peak height and small background, and the parameters lead to reliability factors of 22·1 % for the $0kl$ data and 18·1 % for the $h0l$ data. On the other hand, the author reported that the $hk0$ data were quite troublesome; even after 15 Fourier refinements the projection showed large variations in peak height and a considerable amount of false detail. The reliability factor for the $hk0$ data was calculated to be 30·8 %. The author attributed the poor agreement on this zone to large absorption errors in the photographs, which were taken by the Weissenberg multiple-film technique using copper radiation; the other two zones were photographed with a precession camera using molybdenum radiation. However, the absorption coefficient of selenium is only 12 % greater for copper radiation than it is for molybdenum radiation. Moreover, Lorentz and polarization effects would tend to increase the usefulness of the copper photographs at high values of sin θ; the amount of data obtained from a copper Weissenberg photograph is about the same as that obtained from a molybdenum precession photograph, and the latter subjects the reflections of higher index to unfavorable Lorentz and polarization factors. It thus seems inappropriate to expect that the $hk0$ data would be less reliable than those from the other two zones.

It was soon noticed that the β selenium molecule becomes an eight-membered ring if the y parameter for atom 1 is given the value 0·318 ($= \frac{1}{2}-0\cdot182$), rather than the value 0·182 chosen by the author.

β-Se molecule
(Burbank)

α-Se molecule
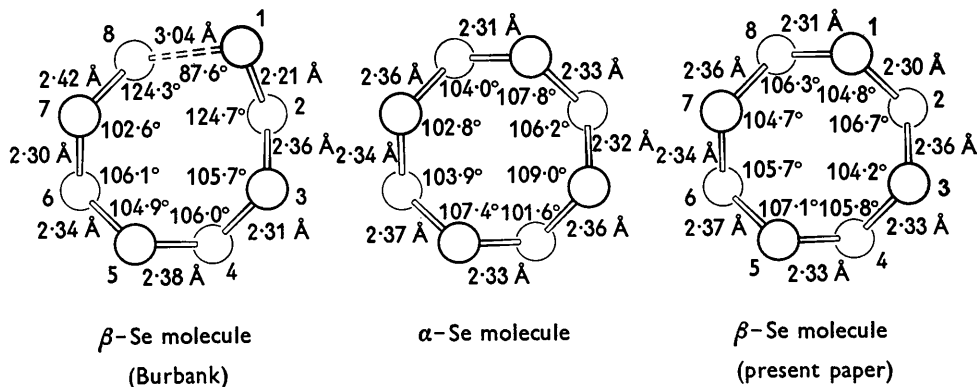
β-Se molecule
(present paper)

Fig. 1.

With this change in parameter, the distance between atoms 8 and 1 becomes 2·30 Å, and that between atoms 1 and 2 becomes 2·32 Å, both of which are equal to the single-bond distance 2·34 Å to within the experimental error. The calculated bond angles are then $\alpha_8 = 106\cdot8$, $\alpha_1 = 106\cdot0$, and $\alpha_2 = 105\cdot0°$, all of which are close to the average value 105·3° found in α selenium.

This change does not, however, have any effect on the short packing distances 2·85 and 2·86 Å, since these do not involve atom 1. It was noticed that the packing would be improved by interchanging the two-fold screw axes and the centers of symmetry in the $h0l$ projection; that is, by moving the origin by $\frac{1}{4}$ in the x direction. This change in origin increases the minimum intermolecular Se–Se distance to 3·50 Å, which is within experimental error of the shortest value 3·53 Å found in α selenium.

Neither of these changes affects the calculated intensities of the type $h0l$, since these reflections occur only when $h = 2n$; however, the signs of the structure factors for $h = 4n+2$ are reversed by the change in origin. Similarly, the symmetry of the projection along the a axis requires that each maximum at y, z be accompanied by an identical maximum at $\frac{1}{2}-y, z$; thus the proposed change in the y parameter of atom 1 cannot be observed from data of the type $0kl$. This zone, of course, is insensitive to the x parameters. Hence the only zonal data which are affected by the proposed parameters changes are those of the type $hk0$; indeed, these are affected only when h is odd. Since the $hk0$ data proved to be so troublesome to Burbank, there seemed to be little doubt that the two revisions—change in the y parameter of atom 1 and addition of 0·250 to the x coordinates of all eight atoms in the asymmetric unit—were needed.

The revisions could, of course, be confirmed by a comparison of calculated and observed structure factors for $hk0$ reflections. Unfortunately, the $hk0$ data were not included in the table of structure factors given by Burbank. However, reproductions of Weissenberg photographs about the c axis were published, and we found that the zero-layer reproduction could

be used in conjunction with a set of c-axis oscillation photographs of much lower intensity prepared eighteen years ago by one of us (J. D. McC.) to provide the intensity data. The intensities were estimated by comparison with a standard strip. Values for the 61 strongest reflections were obtained from the oscillation photographs, while those for the 41 weak reflections were obtained from the Weissenberg reproduction. These intensities, although undoubtedly of considerably less accuracy than multiple-film Weissenberg photographs would have afforded, were judged to be accurate enough to distinguish between the correct and incorrect structures; indeed, the final R factor indicated them to be slightly better than those ob-
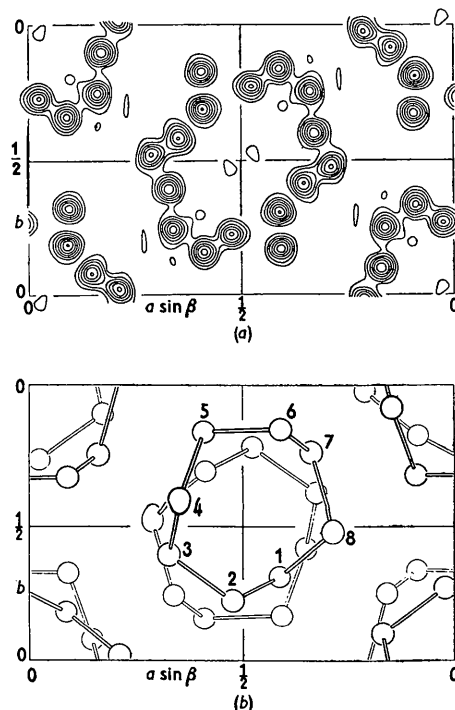

Fig. 2. (a) Electron density of β selenium projected along the c axis. Contours are drawn at intervals of 10 e.Å^{-2}, beginning with 10 e.Å^{-2} line. (b) Crystal structure of β selenium projected along the c axis.

Table 1. *Parameters for β selenium*

Atom	Proposed by R. Burbank			h0l after backshift		hk0 after backshift		Final		
	x	y	z	x	z	x	y	x	y	z
1	0·334	0·182	0·436	0·582	0·437	0·587	0·315	0·584	0·315	0·437
2	0·227	0·221	0·245	0·478	0·246	0·476	0·227	0·477	0·227	0·246
3	0·080	0·397	0·238	0·329	0·240	0·327	0·398	0·328	0·398	0·240
4	0·102	0·578	0·050	0·352	0·050	0·352	0·580	0·352	0·580	0·050
5	0·159	0·832	0·157	0·411	0·157	0·409	0·831	0·410	0·831	0·157
6	0·340	0·832	0·141	0·591	0·142	0·590	0·840	0·590	0·840	0·142
7	0·409	0·763	0·366	0·659	0·368	0·662	0·754	0·660	0·754	0·368
8	0·459	0·476	0·336	0·710	0·334	0·711	0·479	0·710	0·479	0·334

Table 2. *Calculated and observed structure factors for β selenium*

h	F_c	F_o	F_{RB}
h00			
2	20	29	−23
4	−242	223	−253
6	31	37	−35
8	−95	92	−85
10	60	62	−55
12	154	128	152
14	32	42	−34
16	−137	117	−141
h10			
1	59	49	−87
2	40	46	44
3	−257	181	147
4	−127	130	118
5	180	187	168
6	71	93	63
7	29	39	31
8	193	190	−195
9	−49	58	−44
10	25	< 24	24
11	−49	55	−127
12	50	< 23	40
13	22	< 26	−53
14	40	42	44
15	21	< 22	6
16	−37	21	32
h20			
0	−207	149	−208
1	−64	52	−64
2	−261	179	259
3	−114	112	−112
4	72	88	74
5	−43	53	26
6	51	76	−61
7	60	63	−94
8	− 6	21	−10
9	−21	22	− 5
10	−13	26	16
11	− 6	< 27	101
12	−117	127	−115
13	−31	44	6
14	40	47	−39
15	−72	55	−51
16	46	30	47
h30			
1	140	103	167
2	−102	88	−119
3	−25	25	− 6
4	59	49	−49
5	− 6	33	− 2
6	− 3	< 21	− 4
7	−81	105	15
8	−130	118	107
9	94	89	−115
10	−96	80	−87
11	22	< 25	26
12	42	41	−36
13	1	< 24	−13
14	−34	18	−32
15	−15	16	−32
h40			
0	24	36	17
1	−11	< 17	24
2	−23	< 18	23
3	87	85	84
4	142	161	131
5	78	76	−146
6	90	85	−81
7	19	29	−47
8	24	39	20
9	−46	43	− 8
10	−15	< 23	9
11	− 7	< 25	− 2
12	−70	80	−70
13	78	66	39
14	24	23	−24
15	− 4	< 14	14
h50			
1	−100	100	107
2	33	30	30
3	54	68	58
4	52	49	−69
5	−19	30	−52
6	6	< 22	− 6
7	−126	129	−107
8	64	66	−44
9	70	80	62
10	−21	< 25	−25
11	−21	< 25	−36
12	27	39	−26
13	−14	18	1
14	47	38	47
h60			
0	3	< 23	22
1	−100	75	72
2	63	62	−74
3	− 6	< 24	−52
4	− 3	< 24	− 4
5	− 8	< 26	−10
6	−265	255	255
7	−64	66	−41
8	−39	34	−41
9	3	< 25	−26
10	153	152	−155
11	−16	< 22	−29
12	5	18	11
13	−18	< 16	5
h70			
1	−37	32	86
2	−138	147	−126
3	65	80	9
4	37	43	−49
5	106	130	−86
6	−52	35	−44
7	1	< 26	2
8	0	< 21	− 1
9	25	35	−11
10	45	31	43
11	−31	52	50
12	−21	27	10
h80			
0	− 5	31	−42
1	−35	41	−80
2	−52	64	58
3	42	63	32
4	50	63	50
5	− 1	< 25	15
6	95	115	−92
7	8	< 22	−42
8	− 5	< 20	− 4
9	75	69	−72
10	−24	40	30
h90			
1	16	< 23	−14
2	71	54	43
3	−57	54	−30
4	37	32	−23
5	−36	52	61
6	−51	39	−54
7	−48	47	16
h,10,0			
0	− 3	< 16	9
1	− 5	< 16	9
2	−20	15	6
3	26	< 15	−79
4	11	< 12	10

tained by Burbank from the multiple-film precession photographs about the other two axes.

A Fourier projection along the c axis was prepared from the observed structure factors, using signs calculated on the basis of the revised parameters. This Fourier projection is shown in Fig. 2. There is little false detail, the peaks are of nearly uniform height, and there are no large negative regions. The comparison between this projection and that prepared by Burbank on the basis of his structure is striking.

In order to obtain more accurate values for the x and y parameters a back-shift Fourier projection was prepared using calculated structure factors for all observed reflections; the indicated back-shift corrections were then applied to the parameters obtained from the observed Fourier projection. The projections were carried out with the aid of Beevers–Lipson strips, and the peak maxima were located analytically by passing least-squares Gaussian functions through the nine points of electron density surrounding the maxima (Donohue & Carpenter, 1950). A back-shift Fourier on (010) was also prepared, using the calculated structure factors of Burbank, since this apparently had not been done previously. On each zone the average back-shift was approximately 0·01 Å.

No attempt was made to improve the a-axis projection of Burbank, since overlap of peaks is too serious to allow accurate determination of parameters; the final y and z parameters were taken from the c- and b-axis projections, respectively, and the final x parameters were taken as the averages of the values obtained from these two projections. In Table 1 there are listed the parameters obtained from the various projections, as well as the final values. The probable error in these parameters is estimated to correspond to about 0·02 Å; the error could undoubtedly be reduced by the consideration of complete 3-dimensional data.

In Table 2 there are listed the final calculated and observed structure factors for the $hk0$ data; the values calculated for the structure proposed by Burbank are also included. The atomic scattering factors used for selenium were the Thomas–Fermi values compiled by James & Brindley (1935). The calculated $h00$ and $0k0$ structure factors were placed on the same scale as the corresponding ones calculated by Burbank (and which were included in his structure factor table of $h0l$ and $0kl$ data) by applying an empirical temperature factor with $B = 2\cdot0$ Å^2; this is close to the value 2·1 reported by Burbank in α selenium.

Since the magnitudes of the $hk0$ structure factors are appreciably changed by the parameter revision only when h is odd, reliability factors have been calculated both for h even and for h odd; the resulting values are 0·176 and 1·174, respectively, with unobserved reflections omitted. The corresponding values calculated for the structure proposed by Burbank are 0·189 and 0·408. The small improvement in the factor for even h is due principally to shifts in the y para-

meters of atoms 2, 6, and 7, whereas the great improvement for odd h is due to the addition of 0·25 to the x parameters of all the atoms together with the revision of the y parameter of atom 1.

Discussion of the results

The intramolecular bond distances and angles for β selenium are given in Table 3. The average value for the Se–Se bond distance is 2·34 Å, with an average deviation of 0·014 Å; the average bond angle is 105·7°, with an average deviation of 0·8°. These results are in essentially exact agreement with those obtained for α selenium, where the average bond distance is

Table 3. *Bond distances and angles in β selenium*

Atoms	Distances (Å)	Atoms	Angles (°)
1–2	2·30	8–1–2	104·8
2–3	2·36	1–2–3	106·7
3–4	2·33	2–3–4	104·2
4–5	2·33	3–4–5	105·8
5–6	2·37	4–5–6	107·1
6–7	2·34	5–6–7	105·7
7–8	2·36	6–7–8	104·7
8–1	2·31	7–8–1	106·3

2·34±0·02 Å and the average bond angle is 105·3±2·3° (both uncertainties are average deviations). The average deviation in bond length is less than the estimated probable error, 0·03 Å; the maximum deviation, 0·04 Å, is well within the limit of error. Thus all bond distances, as well as all bond angles, are equal within experimental error.

If atoms 1, 3, 5, and 7 are fitted to a plane by least-squares methods, the average deviation of these atoms from the plane is 0·04 Å; the average deviation of atoms 2, 4, 6, and 8 from their best plane is less

Table 4. *Interatomic distances between molecules*

β Selenium		α Selenium	
Atoms	Distance (Å)	Atoms	Distance (Å)
5–8‴	3·48	4–7″	3·53
3–8‴	3·53	6–7‴	3·57
4–6‴	3·58	3–6″	3·61
7–8″	3·64	3–5′	3·64
2–4′	3·66	2–7‴	3·68
1–7″	3·70	4–6″	3·69
4–4′	3·70	3–7′	3·72
1–7′	3·75	5–5′	3·74
4–8′	3·77	1–4‴	3·75
3–7‴	3·77	2–3′	3·78
3–6‴	3·79	5–7′	3·78
2–6′	3·83	1–2‴	3·84
3–7′	3·85	1–8‴	3·84
4–6′	3·85	1–5′	3·86
5–6′	3·86	1–6‴	3·88
1–1′	3·90	3–8″	3·89
1–3′	3·91	3–7″	3·93
5–7‴	3·92	1–4″	3·97
2–8‴	3·94	2–8‴	3·98
2–5′	3·95	3–6′	3·98
1–5′	3·96	4–8‴	3·98
		4–7′	3·99

than 0·01 Å. These two planes are parallel to within 0·5°. Atoms 1, 3, 5, and 7 form a nearly perfect square, as do atoms 2, 4, 6, and 8. To within experimental error the molecule has the symmetry $\bar{8}2m$, as was found for α selenium.

The non-bonded interatomic distances of less than 4·0 Å are given in Table 4, together with those for α selenium. The similarity is remarkable; thus, from an intermolecular as well as an intramolecular standpoint the structures of the two monoclinic forms of selenium show striking resemblance.

Transition to metallic selenium

The conclusion of Burbank that a single crystal of β selenium can transform directly to a single crystal of hexagonal selenium is also apparently in error. The space-group symmetry of hexagonal selenium is that of the enantiomorphic pair $C3_12-D_3^4$ and $C3_22-D_3^6$. Weissenberg photographs of single hexagonal crystals grown from the vapor show the symmetry D_{3d} expected for the point-group $32-D_3$. Weissenberg photographs of transformed β selenium crystals, however, show the higher symmetry, D_{6h}. This difference in symmetry is clearly shown on the first-layer c-axis Weissenberg photographs of a true single hexagonal crystal and of a transformed β selenium crystal reproduced in Fig. 3.

A more reasonable explanation of the observed facts is that the β selenium crystal transforms a small portion at a time (perhaps a few unit cells), the new hexagonal crystallites being oriented in either of two ways with respect to the axes of the β crystal and containing at random either 3_1 or 3_2 screw axes. The diffuseness of the spots of the transformed crystal, causing reflections which are much larger than those from the original β selenium crystal, is also contradictory to the assumption that a single crystal is formed.

The α selenium crystals also undergo spontaneous transformation to the hexagonal form at room temperature, but at a much lower rate than that of the β selenium crystals. In this case the hexagonal crystallites show a preferred orientation with their c-axes parallel to the $[11\bar{1}]$ zone of the mother α selenium crystal. There is also a randomly oriented fraction in this case, which gives rise to a powder pattern of hexagonal selenium. Preferential alignment along $[11\bar{1}]$ is probably in part due to the fact that the identity distance along this axis, 17·29 Å, is close to $\frac{7}{2}$ times the length of the c axis of the hexagonal modification ($\frac{7}{2}$ of 4·952 Å = 17·33 Å). If this were the only factor, however, one might expect alignment
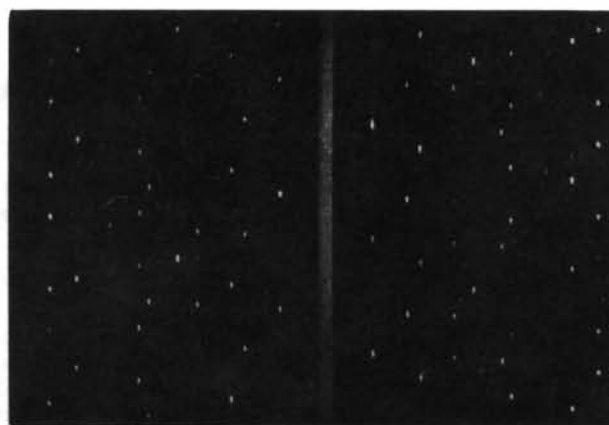
(a)
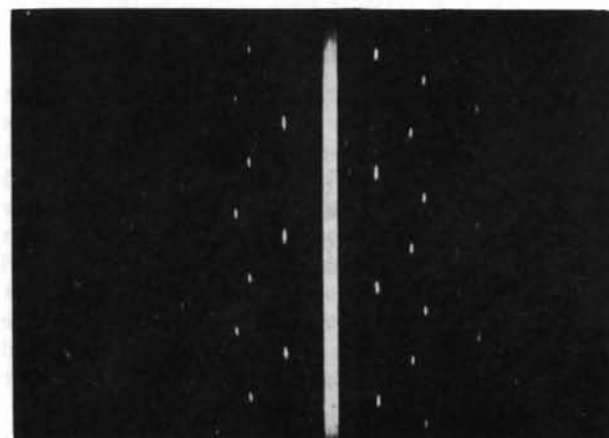
(b)

Fig. 3. (a) Weissenberg photograph of first layer about c axis of a true single crystal of hexagonal selenium. (b) Weissenberg photograph of first layer about c axis of a transformed β selenium crystal.

along $[10\bar{1}]$, the identity distance along which is close to $3c_0$ of the hexagonal form.

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References

BURBANK, R. D. (1951). Acta Cryst. **4**, 140.
BURBANK, R. D. (1952). Acta Cryst. **5**, 236.
DONOHUE, J. & CARPENTER, G. B. (1950). J. Amer. Chem. Soc. **72**, 2315.
JAMES, R. W. & BRINDLEY, G. W. (1935); in International Tables for the Determination of Crystal Structures, vol. 2, p. 572. Berlin: Borntraeger.