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# The Crystal Structure of β-Monoclinic Selenium*

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The crystal structure of β-monoclinic selenium has been determined by the application of the Harker–Kasper phase inequalities and two-dimensional Fourier syntheses. The β-selenium molecule is an eight-membered chain with the configuration of a puckered ring molecule in which one of the bonds has been broken. At one end of the chain the terminal atom and its neighbor are nearly double-bonded. The remaining six bonds in the chain are approximately single bonds. At several points in each molecule there are unusually strong interactions with neighboring molecules. About 7·7 electron pairs are utilized for bonding within the molecule while 0·3 electron pairs are engaged in intermolecular bonding.

Diffraction data have been obtained which demonstrate that a single crystal of β-selenium can transform directly into a single crystal of metallic selenium. During the transition the molecules are broken down into smaller fragments which recombine to form the infinitely long helical chains of metallic selenium.

Relations between mixed crystals of sulfur and selenium, and between the various polymorphs of selenium are discussed.

## Introduction

The first observations on β-monoclinic selenium were made by Muthmann (1890) in the course of an investigation of the crystallography of sulfur and selenium. He was able to identify two red monoclinic modifications in a preparation of crystals obtained by evaporating a solution of vitreous selenium in carbon disulfide. Although a careful goniometric study was made of the second polymorph, the work has been ignored or distrusted by most subsequent investigators. However, Muthmann's discovery was well validated by Klug (1934) who made a study with X-rays and obtained unit cell constants in good agreement with the classical measurements.

The present paper which presents the structure determination of β-monoclinic selenium is the second and concluding part of a study on the crystal chemistry of the element selenium. The first paper on the structure of α-monoclinic selenium (Burbank, 1951) served as a guide for all phases of the present work and contains a number of working details which have not been repeated in the present account.

## Experimental

Crystals of β-selenium were obtained by controlling the rate of evaporation of a saturated solution of vitreous selenium in carbon disulfide. A half liter of solution was first allowed to decrease in volume by 10% over a 72 hr. period at room temperature. A large crop of α crystals was produced and filtered from the solution. The volume of the solution was then decreased by 75% over a second 72 hr. period at room temperature. The new crop of crystals contained both monoclinic polymorphs. The β crystals were present in a variety of habits similar to those described by Muthmann (1890). A chunky prismatic habit with dimensions not exceeding 0·5 mm. was predominant.

Crystals less than 0·1 mm. in all dimensions were chosen for X-ray examination to minimize serious absorption errors ($\mu$ for Mo $K\alpha$ radiation is 330 cm.$^{-1}$) From measurements with a precession camera (Buerger, 1944) using Mo $K\alpha$ radiation, $\lambda = 0{\cdot}7107$ Å, the unit cell constants are found to be

$$a = 12{\cdot}85 \pm 0{\cdot}01,\ b = 8{\cdot}07 \pm 0{\cdot}01,\ c = 9{\cdot}31 \pm 0{\cdot}01 \text{ Å},$$
$$\beta = 93^\circ\, 8' \pm 5';$$
space group, $P2_1/a$;
number of atoms in cell = 32 ,

in good agreement with the earlier measurements of Klug (1934).

Intensity data were recorded by multiple exposures with the precession camera using Mo $K\alpha$ radiation, and by multiple film technique with the Weissenberg camera using Cu $K\alpha$ radiation. The intensities were measured by visual comparison and corrected for the Lorentz and polarization factors but not for absorption. The observed structure factors are estimated to be in error by about ±15%.

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Table 1. *Original and corrected unitary structure amplitudes for β-selenium*

Corrected values obtained from the relation $U^{*}_{h0l} = U_{h0l} \exp \{1{\cdot}6[(\sin \theta)/\lambda]^2\}$.

| Group 1 | | | Group 2 | | | Group 3 | | | Group 4 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $H$ | $U_H$ | $U^{*}_H$ | $H$ | $U_H$ | $U^{*}_H$ | $H$ | $U_H$ | $U^{*}_H$ | $H$ | $U_H$ | $U^{*}_H$ |
| $60\bar{4}$ | 0·40 | 0·46 | 16,0,0 | 0·50 | 0·93 | 607 | 0·66 | 0·91 | 405 | 0·41 | 0·48 |
| 202 | 0·29 | 0·30 | 0,0,10 | 0·50 | 0·80 | $60\bar{3}$ | 0·48 | 0·54 | $12,0,\bar{7}$ | 0·36 | 0·62 |
| 14,0,2 | 0·29 | 0·48 | 402 | 0·33 | 0·35 | 203 | 0·44 | 0·46 | 12,0,3 | 0·35 | 0·53 |
| $20\bar{2}$ | 0·27 | 0·28 | $4,0,\overline{10}$ | 0·32 | 0·52 | $14,0,\bar{3}$ | 0·41 | 0·68 | 805 | 0·34 | 0·45 |
| $10,0,\bar{6}$ | 0·27 | 0·40 | 8,0,10 | 0·32 | 0·60 | $10,0,\bar{3}$ | 0·36 | 0·47 | $80\bar{5}$ | 0·31 | 0·40 |
| 606 | 0·25 | 0·33 | 12,0,0 | 0·30 | 0·43 | $10,0,\bar{7}$ | 0·33 | 0·51 | 801 | 0·31 | 0·37 |
| $20\bar{6}$ | 0·22 | 0·26 | 404 | 0·28 | 0·32 | 205 | 0·30 | 0·34 | $8,0,\overline{11}$ | 0·23 | 0·45 |
| 10,0,4 | 0·22 | 0·31 | 400 | 0·27 | 0·28 | 207 | 0·23 | 0·29 | $40\bar{5}$ | 0·22 | 0·26 |
| $2,0,\overline{12}$ | 0·18 | 0·35 | $8,0,\overline{10}$ | 0·27 | 0·48 | 603 | 0·22 | 0·25 | $12,0,\bar{5}$ | 0·22 | 0·34 |
| $60\bar{6}$ | 0·18 | 0·23 | $12,0,\bar{8}$ | 0·25 | 0·46 | 10,0,7 | 0·22 | 0·36 | 12,0,1 | 0·21 | 0·30 |
| 608 | 0·18 | 0·27 | 002 | 0·20 | 0·20 | 10,0,9 | 0·22 | 0·42 | $80\bar{9}$ | 0·18 | 0·30 |
| $60\bar{8}$ | 0·17 | 0·24 | 4,0,12 | 0·18 | 0·37 | $20\bar{7}$ | 0·20 | 0·25 | 409 | 0·17 | 0·26 |
| 208 | 0·16 | 0·22 | 16,0,4 | 0·18 | 0·37 | $20\bar{5}$ | 0·20 | 0·23 | $40\bar{3}$ | 0·16 | 0·17 |
| 14,0,0 | 0·14 | 0·23 | 804 | 0·16 | 0·20 | $60\bar{7}$ | 0·20 | 0·27 | $80\bar{1}$ | 0·15 | 0·18 |
| $14,0,\bar{4}$ | 0·14 | 0·24 | $40\bar{8}$ | 0·15 | 0·21 | 605 | 0·15 | 0·19 | $40\bar{1}$ | 0·13 | 0·14 |
| 14,0,6 | 0·14 | 0·27 | $40\bar{6}$ | 0·14 | 0·17 | $14,0,\bar{5}$ | 0·15 | 0·26 | $12,0,\bar{9}$ | 0·13 | 0·26 |
| 10,0,0 | 0·13 | 0·17 | 16,0,2 | 0·13 | 0·25 | $10,0,\bar{5}$ | 0·12 | 0·17 | 16,0,1 | 0·13 | 0·24 |
| 2,0,12 | 0·13 | 0·26 | 800 | 0·12 | 0·14 | $14,0,\bar{1}$ | 0·10 | 0·16 | 0,0,11 | 0·11 | 0·19 |
| $60\bar{2}$ | 0·13 | 0·14 | 12,0,4 | 0·12 | 0·19 | $60\bar{9}$ | 0·09 | 0·14 | $40\bar{7}$ | 0·11 | 0·14 |
| 10,0,6 | 0·13 | 0·20 | 12,0,2 | 0·11 | 0·16 | 201 | 0·06 | 0·06 | $12,0,\bar{1}$ | 0·10 | 0·14 |
| 204 | 0·12 | 0·13 | 004 | 0·10 | 0·11 | 10,0,3 | 0·06 | 0·08 | 005 | 0·09 | 0·10 |
| 602 | 0·12 | 0·13 | $12,0,\bar{6}$ | 0·10 | 0·16 | $20\bar{1}$ | 0·05 | 0·05 | $40\bar{9}$ | 0·08 | 0·12 |
| $10,0,\bar{8}$ | 0·11 | 0·18 | 406 | 0·08 | 0·10 | 14,0,1 | 0·05 | 0·08 | $12,0,\bar{3}$ | 0·08 | 0·12 |
| 10,0,2 | 0·10 | 0·13 | 802 | 0·08 | 0·10 | $60\bar{5}$ | 0·04 | 0·05 | $16,0,\bar{1}$ | 0·06 | 0·11 |
| 604 | 0·09 | 0·11 | 408 | 0·07 | 0·10 | $10,0,\bar{1}$ | 0·04 | 0·05 | 009 | 0·04 | 0·06 |
| $10,0,\bar{2}$ | 0·09 | 0·12 | 806 | 0·07 | 0·10 | $20\bar{3}$ | 0·03 | 0·03 | 401 | 0·04 | 0·04 |
| 6,0,10 | 0·06 | 0·11 | 008 | 0·06 | 0·08 | | | | $80\bar{3}$ | 0·04 | 0·05 |
| $10,0,\bar{4}$ | 0·06 | 0·08 | 12,0,6 | 0·06 | 0·10 | | | | | | |
| 200 | 0·04 | 0·04 | $80\bar{2}$ | 0·04 | 0·05 | | | | | | |
| $20\bar{8}$ | 0·04 | 0·05 | $40\bar{4}$ | 0·03 | 0·03 | | | | | | |
| | | | $40\bar{2}$ | 0·02 | 0·02 | | | | | | |

Zero values of $U$ were found for 600; $2,0,\overline{10}$; $20\bar{4}$; 206; 2,0,10; $6,0,\overline{10}$; $10,0,\overline{10}$; 10,0,8; $14,0,\bar{6}$; $14,0,\bar{2}$ and 14,0,4 in Group 1, for 006; 0,0,12; $4,0,\overline{12}$; 4,0,10; $80\bar{8}$; $80\bar{6}$; $80\bar{4}$; 808; $12,0,\bar{4}$; $12,0,\bar{2}$; $16,0,\bar{4}$ and $16,0,\bar{2}$ in Group 2, for $2,0,\overline{11}$; $20\bar{9}$; 209; 2,0,11; $6,0,\overline{11}$; $60\bar{1}$; 601; 609; $10,0,\bar{9}$; 10,0,1; 10,0,5; $14,0,\bar{7}$; 14,0,3 and 14,0,5 in Group 3 and for 001; 003; 007; $4,0,\overline{11}$; 403; 407; 4,0,11; $80\bar{7}$; 803; 807; 809; 12,0,5; 12,0,7; $16,0,\bar{5}$; $16,0,\bar{3}$ and 16,0,3 in Group 4.

## Analysis of the *b*-axis projection by the Harker–Kasper phase inequalities

In the determination of the structure of α-selenium (Burbank, 1951) the Harker–Kasper phase inequalities (Harker & Kasper, 1947, 1948) were successfully applied after other methods had proven difficult. Guided by this experience, the analysis of β-selenium proceeded on the premise that the immediate use of the phase inequalities would be the most practical approach.

The structure factors for the three principal zones were placed on an absolute scale by the method of averaging which has been described by Wilson (1942) and by Harker (1948). Then, the structure factors on an absolute scale were converted to unitary structure amplitudes, $U_{hkl}$, by dividing by the sum of the atomic scattering factors in the unit cell. The unitary structure amplitudes for each zone were examined for large values and the $h0l$ reflections were selected for application of the inequalities.

The procedure used for applying the inequalities differs from the work of Kasper, Lucht & Harker (1950) on decaborane. Instead of using general $hkl$ reflections, only data from one zone are considered. For such a special class of reflections the simplest of the addition–subtraction relations is of great importance. In the notation of Gillis (1948) we have

$$(U_H \pm_{H'})^2 \leq (1 \pm U_{H+H'})(1 \pm U_{H-H'}) \,, \qquad (1)$$

where $U_H$ stands for $U_{hkl}$, $U_{H'}$ stands for $U_{h'k'l'}$, etc., and the inequality is applicable to any centrosymmetric projection.

For the inequality to yield a practical number of conclusions the unitary structure amplitudes must first be multiplied by a factor of the form $\exp\{M[(\sin\theta)/\lambda]^2\}$, where $M$ is a positive number. One does not have to think solely of the effect of thermal vibrations in justifying the use of this correction. In terms of structure-factor calculations it is equivalent to making small adjustments in the atomic co-ordinates which may cause a high-order set of planes to increase its reflecting power to a large value, while at the same time low-order planes remain almost unaffected. The signs of the low-order planes are often the critical ones that must be known for a Fourier series to converge. The values of these signs

Table 2. *Signs of β-selenium h0l reflections as derived from the inequalities*

| $H$ | $U^*_H$ | Sign | $H$ | $U^*_H$ | Sign | $H$ | $U^*_H$ | Sign | $H$ | $U^*_H$ | Sign |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 200 | 0·04 | $-bc$ | 204 | 0·13 | $-bc$ | $60\bar{3}$ | 0·54 | $-b$ | $10,0,\bar{3}$ | 0·47 | $b$ |
| 400 | 0·28 | $-1$ | 205 | 0·34 | $-b$ | $60\bar{2}$ | 0·14 | $a$* | 10,0,2 | 0·13 | $-a$ |
| 800 | 0·14 | $-1$ | 207 | 0·29 | $-b$ | 603 | 0·25 | $-b$ | 10,0,3 | 0·08 | $b$ |
| 10,0,0 | 0·17 | $-bc$ | 208 | 0·22 | $a$ | 605 | 0·19 | $-b$ | 10,0,4 | 0·31 | $bc$ |
| 12,0,0 | 0·43 | $+1$ | $4,0,\overline{10}$ | 0·52 | $+1$ | 606 | 0·33 | $bc$ | 10,0,6 | 0·20 | $a$ |
| 16,0,0 | 0·93 | $-1$ | $40\bar{8}$ | 0·21 | $+1$ | 607 | 0·91 | $b$ | $12,0,\bar{8}$ | 0·46 | $+1$ |
| 002 | 0·20 | $-1$ | $40\bar{7}$ | 0·14 | $-c$ | $8,0,\overline{11}$ | 0·45 | $c$ | $12,0,\bar{7}$ | 0·62 | $c$ |
| 004 | 0·11 | $-1$ | $40\bar{6}$ | 0·17 | $-1$ | $8,0,\overline{10}$ | 0·48 | $-1$ | $12,0,\bar{6}$ | 0·16 | $-1$ |
| 008 | 0·08 | $+1$ | $40\bar{5}$ | 0·26 | $-ab$ | $80\bar{9}$ | 0·30 | $-c$ | $12,0,\bar{5}$ | 0·34 | $-ab$ |
| 0,0,10 | 0·80 | $-1$ | $40\bar{4}$ | 0·03 | $+1$ | $80\bar{5}$ | 0·40 | $ab$ | 12,0,1 | 0·30 | $-ab$ |
| 0,0,11 | 0·19 | $-c$ | $40\bar{3}$ | 0·17 | $c$ | $80\bar{1}$ | 0·18 | $-c$ | 12,0,3 | 0·53 | $-c$ |
| $2,0,\overline{12}$ | 0·35 | $a$ | $40\bar{1}$ | 0·14 | $ab$ | 801 | 0·37 | $c$ | 12,0,4 | 0·19 | $-1$ |
| $20\bar{8}$ | 0·05 | $-bc$* | 402 | 0·35 | $-1$ | 802 | 0·10 | $+1$ | $14,0,\bar{5}$ | 0·26 | $b$ |
| $20\bar{7}$ | 0·25 | $-b$ | 404 | 0·32 | $+1$ | 805 | 0·45 | $-ab$ | $14,0,\bar{4}$ | 0·24 | $bc$ |
| $20\bar{6}$ | 0·26 | $bc$ | 405 | 0·48 | $ab$ | 8,0,10 | 0·60 | $+1$ | $14,0,\bar{3}$ | 0·68 | $-b$ |
| $20\bar{5}$ | 0·23 | $b$ | 409 | 0·26 | $-ab$ | $10,0,\bar{7}$ | 0·51 | $-b$ | 14,0,2 | 0·48 | $a$ |
| $20\bar{2}$ | 0·28 | $-a$ | $60\bar{7}$ | 0·27 | $b$ | $10,0,\bar{6}$ | 0·40 | $-bc$ | 16,0,2 | 0·25 | $+1$ |
| 202 | 0·30 | $a$ | $60\bar{6}$ | 0·23 | $-a$ | $10,0,\bar{5}$ | 0·17 | $b$ | 16,0,4 | 0·37 | $+1$ |
| 203 | 0·46 | $b$ | $60\bar{4}$ | 0·46 | $-bc$ | | | | | | |

* Incorrect signs as judged by comparison with final structure.

Table 3. *Coefficients for the first Fourier synthesis of β-selenium*

| Group 1 | | | Group 2 | | | Group 3 | | | Group 4 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $h0l$ | $\lvert F\rvert$ | Sign | $h0l$ | $\lvert F\rvert$ | Sign | $h0l$ | $\lvert F\rvert$ | Sign | $h0l$ | $\lvert F\rvert$ | Sign |
| 202 | 311 | $-1$ | 402 | 316 | $-1$ | 203 | 429 | $+1$ | 405 | 284 | $-1$ |
| $20\bar{2}$ | 304 | $+1$ | 400 | 279 | $-1$ | $60\bar{3}$ | 372 | $-1$ | 801 | 213 | $+c$ |
| $60\bar{4}$ | 286 | $-c$ | 002 | 234 | $-1$ | 607 | 302 | $+1$ | 805 | 170 | $+1$ |
| $20\bar{6}$ | 148 | $+c$ | 404 | 220 | $+1$ | 205 | 225 | $-1$ | $80\bar{5}$ | 166 | $-1$ |
| 606 | 134 | $+c$ | 0,0,10 | 170 | $-1$ | $10,0,\bar{3}$ | 188 | $+1$ | $40\bar{5}$ | 157 | $+1$ |
| $10,0,\bar{6}$ | 109 | $-c$ | 12,0,0 | 132 | $+1$ | 603 | 161 | $-1$ | $40\bar{3}$ | 141 | $+c$ |
| $60\bar{2}$ | 107 | $-1$* | 16,0,0 | 123 | $-1$ | $20\bar{5}$ | 157 | $+1$ | 12,0,3 | 134 | $-c$ |
| 204 | 102 | $-c$ | $4,0,\overline{10}$ | 102 | $+1$ | 207 | 129 | $-1$ | $40\bar{1}$ | 132 | $-1$ |
| $60\bar{6}$ | 100 | $+1$ | 004 | 91 | $-1$ | $14,0,\bar{3}$ | 127 | $-1$ | $80\bar{1}$ | 107 | $-c$ |
| 602 | 98 | | 804 | 91 | | $20\bar{7}$ | 116 | $-1$ | $12,0,\bar{7}$ | 100 | $+c$ |
| 10,0,4 | 98 | $+c$ | $40\bar{6}$ | 89 | $-1$ | $10,0,\bar{7}$ | 116 | $-1$ | 12,0,1 | 89 | $+1$ |
| 14,0,2 | 91 | $-1$ | 800 | 84 | $-1$ | $60\bar{7}$ | 95 | $+1$ | $12,0,\bar{5}$ | 77 | $+1$ |
| 208 | 75 | $-1$ | 8,0,10 | 73 | $+1$ | 605 | 89 | $-1$ | 005 | 70 | |
| 10,0,0 | 70 | $-c$ | $8,0,\overline{10}$ | 70 | $-1$ | 201 | 73 | | 409 | 64 | $+1$ |
| $60\bar{8}$ | 70 | | $40\bar{8}$ | 68 | $+1$ | 10,0,7 | 73 | | $40\bar{7}$ | 59 | $-c$ |
| 608 | 70 | | $12,0,\bar{8}$ | 61 | $+1$ | $20\bar{1}$ | 57 | | $80\bar{9}$ | 54 | $-c$ |
| 604 | 61 | | 802 | 54 | $+1$ | $10,0,\bar{5}$ | 54 | $+1$ | $8,0,\overline{11}$ | 50 | $+c$ |
| $10,0,\bar{2}$ | 52 | | 406 | 50 | | 10,0,9 | 50 | | $12,0,\bar{1}$ | 45 | |
| 10,0,2 | 52 | $+1$ | 12,0,2 | 45 | | $14,0,\bar{5}$ | 41 | $+1$ | 401 | 43 | |
| 200 | 48 | $-c$ | 12,0,4 | 41 | $-1$ | $20\bar{3}$ | 34 | | 0,0,11 | 32 | $-c$ |
| 14,0,0 | 45 | | 16,0,4 | 36 | $+1$ | $60\bar{9}$ | 32 | | $40\bar{9}$ | 32 | |
| 10,0,6 | 45 | $-1$ | 4,0,12 | 34 | | $14,0,\bar{1}$ | 32 | | $12,0,\bar{3}$ | 32 | |
| $2,0,\overline{12}$ | 41 | $-1$ | 408 | 32 | | 10,0,3 | 30 | $+1$ | 16,0,1 | 30 | |
| $14,0,\bar{4}$ | 41 | $+c$ | 806 | 32 | | $60\bar{5}$ | 27 | | $80\bar{3}$ | 27 | |
| $10,0,\bar{8}$ | 32 | | $12,0,\bar{6}$ | 32 | $-1$ | $10,0,\bar{1}$ | 20 | | $12,0,\bar{9}$ | 27 | |
| $10,0,\bar{4}$ | 30 | | 008 | 30 | $+1$ | 14,0,1 | 16 | | 009 | 16 | |
| 14,0,6 | 30 | | 16,0,2 | 30 | $+1$ | | | | $16,0,\bar{1}$ | 16 | |
| 2,0,12 | 27 | | $80\bar{2}$ | 27 | | | | | | | |
| $20\bar{8}$ | 23 | $-c$* | $40\bar{4}$ | 25 | $+1$ | | | | | | |
| 6,0,10 | 16 | | $40\bar{2}$ | 20 | | | | | | | |
| | | | 12,0,6 | 16 | | | | | | | |

* Incorrect signs as judged by comparison with final structure.

will not be endangered by the slight shifts in atomic positions used to obtain a few large unitary structure amplitudes. The magnitude of $M$ is limited only by the conditions that no unitary structure amplitude shall exceed unity after correction and that there shall be no mutually inconsistent derivation of signs.

A value of 1·6 for $M$ was found suitable, and the original and corrected unitary structure amplitudes, $U_{h0l}$ and $U^*_{h0l}$, are listed in Table 1. To facilitate using inequality (1) the data are divided into four groups having the property that if two $U$'s are selected from any one group to represent $U_{H+H'}$ and $U_{H-H'}$, then

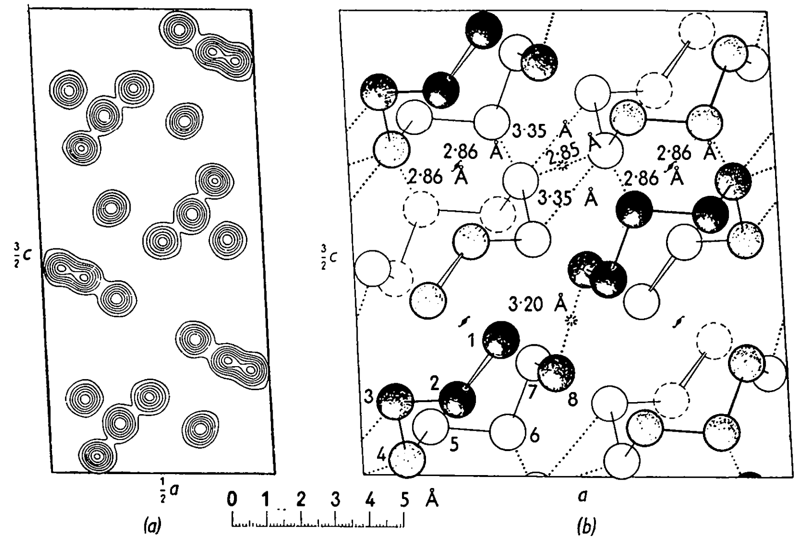

Fig. 1. (a) Electron density of $\beta$-selenium projected along the $b$-axis. Contours at intervals of 10 e.Å$^{-2}$. Lowest contour at 10 e.Å$^{-2}$ level. (b) Crystal structure of $\beta$-selenium projected along the $b$-axis.

the values of the indices are such that $U_H$ and $U_{H'}$, are present somewhere in the four groups.

The systematic application of inequality (1) has been described in the $\alpha$-selenium analysis (Burbank, 1951), and led in the present case to the results which are listed in Table 2. There are 22 direct sign determinations, 33 signs expressed in terms of the unknown signs $a$ and $b$, and 19 signs which involve the unknown sign $c$. The 33 signs which depend on $a$ and $b$ fall in two categories. Reflections with both indices even depend only on $a$, while reflections with an odd index depend on $b$ as well. The structure is independent of $b$ and changing the sign of $b$ merely corresponds to changing the origin of co-ordinates from one center of symmetry to another. Thus we can arbitrarily assign $b$ a positive value but both values of $a$ must be investigated.

The information the inequalities have yielded for Fourier synthesis is illustrated in Table 3 where the $h0l$ structure factors for the four groups of Table 1 are listed. The signs have been evaluated on the assumption that $b = +1$ and $a = -1$. The total weight of all the coefficients is 10,847 while the weight of the coefficients to be used in the first Fourier synthesis is 7,256 or 67% of the total.

Two 55-term syntheses were made, one with $a = +1$, one with $a = -1$. The maps are identical in each case except for the fact that the projected positions of screw axes and symmetry centers are interchanged. Positions were indicated for all eight atoms in the asymmetric unit and six of the peaks were completely resolved. Thus a centrosymmetric projection can be solved directly from the inequalities without any supplementary information. However, a twofold ambiguity remains when discussing the complete structure in three dimensions.

## Remarks on the inequalities

The addition–subtraction relation of inequality (1) can be given an interpretation which is somewhat analogous to a familiar trial-and-error technique. When a few reflections in a zone are close to their maximum possible values one knows that atoms must be located on or near all the sets of planes concerned. The sets of planes must mutually intersect at positions near the atomic sites. Hence if one has a knowledge of the molecular shape he can draw traces of the sets of planes for different sign combinations and hope to find a combination which is consistent with some postulated molecular orientation. Inequality (1) examines the unitary structure amplitudes of a group of four sets of planes. *If the inequality can be violated then three or four sets of planes must mutually intersect and a statement is obtained of the possible sign combinations which the sets of planes can assume.* The inequality is an algebraic device which transcends the graphical investigation of traces of planes because it can be applied to all reflections, large and small, and provides information on many of the less strong reflections in terms of the strongest ones.

It is the writer's conviction that the phase inequalities represent an extremely valuable and, so far, neglected tool. It is advocated that the following procedure be considered before concluding that the method will be useless on a given problem.

Prepare a list of $U$'s from the experimental data and investigate it for any appreciable values that occur. If values greater than 0·7 occur at any scattering angle the situation is very fortunate. If values of the order of 0·4 or larger occur for values of $(\sin\theta)/\lambda$ near 0·5 or 0·6, then the applicability of the method should certainly be investigated by using large correction factors. The time that is necessary to give the inequalities a fair trial is quite modest. As an example, starting with the uncorrected $U$'s of Table 1 a period of seven days was required to obtain the information listed in Table 3.

## Determination of the structure in three dimensions

The inequalities led to two possible structures, one for each value of the unknown sign $a$ of Table 2. Molecules similar in appearance to those of α-selenium were easily recognized in the $b$-axis projections obtained from the two 55-term syntheses. To decide which structure was correct the assumption was made that the β molecule was identical to the α molecule, and scale models were constructed for each possibility. Values for the $y$ parameters were obtained by equalizing the packing distances. Structure factors were calculated for $hk0$ and $0kl$ reflections and the structure with $a = -1$ was chosen on the basis of a superior correlation with the experimental structure factors.

At this stage the unknown sign $c$ could be determined, and 19 more terms were added to form a 74-term synthesis. The refinement proceeded rapidly to the final 114-term synthesis which is shown in Fig. 1 (a). The molecules are well resolved and are inclined at a large angle to the plane of the projection. The $h0l$ structure factors give the usual correlation function a value of 18·1 %.

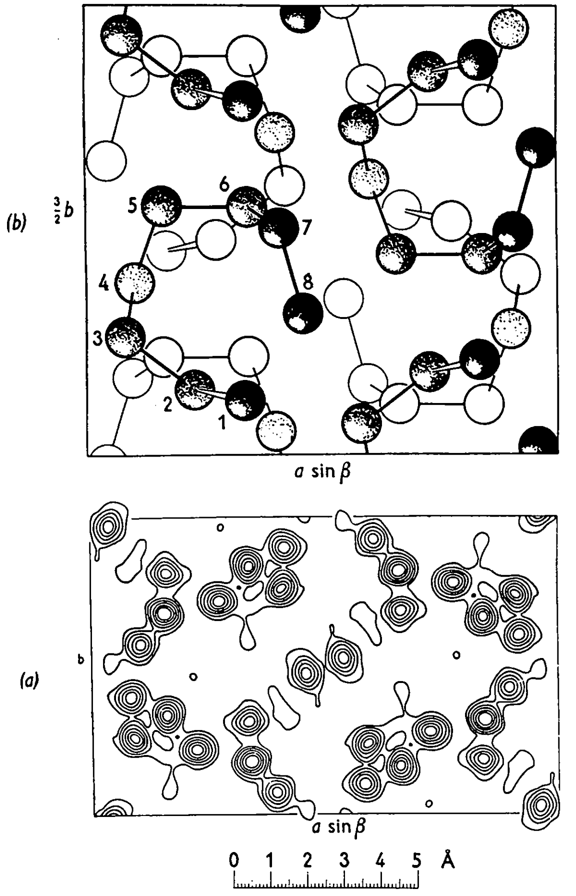

Fig. 2. (a) Electron density of β-selenium projected along the c-axis. Contours at intervals of 10 e.Å$^{-2}$. Lowest contour at 10 e.Å$^{-2}$ level. (b) Crystal structure of β-selenium projected along the c-axis.

In contrast to the $b$-axis projection, which was easily refined, the $c$-axis projection was very troublesome. The $y$ parameters obtained from the scale model were used to compute signs for the first synthesis. Through the kindness of Prof. R. Pepinsky, Pennsylvania State College, the non-negativity method (Eiland & Pepinsky, 1950) was then used with the X-ray analogue computer (Pepinsky, 1947) and the signs of a few more large terms were indicated. The refinement had to be continued by conventional computation and was carried through 15 maps to the result shown in Fig. 2 (a). All the atoms are well resolved, but the peak heights are not as uniform as on the other projections and there is considerably more false detail. The molecules are almost parallel to the plane of the projection and overlap to a considerable extent. For the $hk0$ reflections the correlation function has a value of 30·8 %.

The $hk0$ data were obtained from Weissenberg photographs and are subject to much greater absorption errors than the precession photographs used for the other projections. Consequently, the $a$-axis projection, illustrated in Fig. 3 (a), was used for the final determination of the $y$ parameters. There is overlapping of both atoms and molecules, but this projection is considered more reliable than the $c$-axis projection, first because the map is almost free of false detail, and secondly because of the better correlation of the $0kl$ structure factors which give a value of 22·1 %.

The final $x$ and $z$ parameters obtained from $\varrho(x, z)$ and final $y$ parameters obtained from $\varrho(y, z)$ are listed in Table 4. A comparison of the observed and calculated structure factors for the $h0l$ and $0kl$ reflections is presented in Table 5. The over-all value of the correlation function for these reflections is 18·7 %.

Table 4. *Final parameters for β-selenium*

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| 1 | 0·334 | 0·182 | 0·436 |
| 2 | 0·227 | 0·221 | 0·245 |
| 3 | 0·080 | 0·397 | 0·238 |
| 4 | 0·102 | 0·578 | 0·050 |
| 5 | 0·159 | 0·832 | 0·157 |
| 6 | 0·340 | 0·832 | 0·141 |
| 7 | 0·409 | 0·763 | 0·366 |
| 8 | 0·459 | 0·476 | 0·336 |

If the parameters had been taken from the less suitable projections, namely $\varrho(x, y)$ for $x$, $\varrho(x, y)$ for $y$ and $\varrho(y, z)$ for $z$, the differences $\Delta x$, $\Delta y$, $\Delta z$ against the above values remain under 0·006 in all cases and their sum $\Sigma(|\Delta x|+|\Delta y|+|\Delta z|)$ is 0·078 for β-selenium; this compares with 0·072 for the same sum in α-

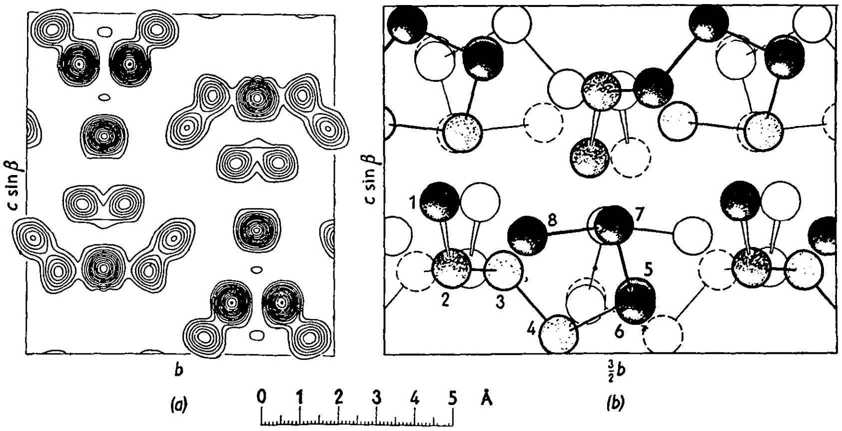

Fig. 3. (a) Electron density of β-selenium projected along the a-axis. Contours at intervals of 10 e.Å$^{-2}$. Lowest contour at 10 e.Å$^{-2}$ level. (b) Crystal structure of β-selenium projected along the a-axis.

selenium. The critical distance $d_{81}$, upon which rests the conclusion that the β molecule is a chain and not a ring, changes by only −0·03 Å.

## Description of the structure

From the parameters of Table 4 the distances between atoms of one molecule are found to be

$$\begin{array}{ll} d_{12} = 2{\cdot}21\ \text{Å} & d_{56} = 2{\cdot}34\ \text{Å} \\ d_{23} = 2{\cdot}36 & d_{67} = 2{\cdot}30 \\ d_{34} = 2{\cdot}31 & d_{78} = 2{\cdot}42 \\ d_{45} = 2{\cdot}38 & d_{81} = 3{\cdot}04 \end{array}$$

where $d_{12}$ is the distance between atoms 1 and 2, etc.

The angles subtended at each atom by its two neighbors in the molecule are found to be

$$\begin{array}{ll} \alpha_1 = 87{\cdot}6^\circ & \alpha_5 = 104{\cdot}9^\circ \\ \alpha_2 = 124{\cdot}7 & \alpha_6 = 106{\cdot}1 \\ \alpha_3 = 105{\cdot}7 & \alpha_7 = 102{\cdot}6 \\ \alpha_4 = 106{\cdot}0 & \alpha_8 = 124{\cdot}3 \end{array}$$

where $\alpha_1$ is the angle subtended at atom 1, etc.

These results are at striking variance with those of the α-selenium analysis, where an eight-membered ring molecule was found, with average bond distances of 2·34 Å and average bond angles of 105·3°. The distance of 2·21 Å between atoms 1 and 2 and the angle of 124·7° subtended at atom 2 indicate that atoms 1 and 2 are nearly double-bonded. The distance of 3·04 Å between atoms 8 and 1 indicates that there is practically no bonding between these atoms. One must conclude 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 of the chain double-bonded to its neighbor while the other terminal atom is single-bonded to its neighbor. Figs. 1(b), 2(b) and 3(b) illustrate the appearance of the molecules on the three principal projections.

Drawings of α and β molecules are compared in Fig. 4. The α molecule has the non-crystallographic point group symmetry $\bar{8}2m$, with four atoms lying in one plane and the remaining four atoms lying in a second parallel plane. Seven of the atoms in the β molecule adhere rather closely to this configuration.

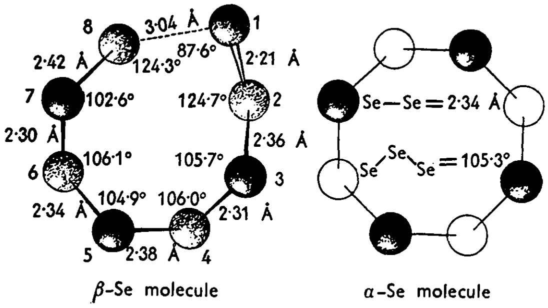

Fig. 4.

Using orthogonal co-ordinates $x'$, $y$ and $z'$ based on the axes $a$, $b$ and $c'$, with $c'$ perpendicular to $a$ and $b$, atoms 3, 5 and 7 define the plane

$$x' - 0{\cdot}69y - 1{\cdot}80z' + 5{\cdot}26 = 0\ ,$$

while atoms 2, 4 and 6 define the plane

$$x' - 0{\cdot}68y - 1{\cdot}91z' + 2{\cdot}77 = 0\ .$$

The two planes are parallel to within 1·7°. The equations of these planes can be averaged to define a new plane

$$x' - 0{\cdot}68y - 1{\cdot}85z' + 4{\cdot}02 = 0\ .$$

Atoms 3, 5 and 7 are equidistant ±0·017 Å to one side of the plane while atoms 2, 4, 6 and 8 are equidistant ±0·017 Å to the other side of the plane.

The preceding description of the β molecule is incomplete and gives no indication of how such a configuration could possibly be stable. There would be charges developed at atoms 8 and 2 and no possibility of resonance. If the double bond shifted

Table 5. *Observed and calculated structure factors for β-selenium*

| *hkl* | $F_o$ | $F_c$ | *hkl* | $F_o$ | $F_c$ | *hkl* | $F_o$ | $F_c$ | *hkl* | $F_o$ | $F_c$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 200 | 48 | −23 | 4,0,10 | < 11 | 0 | 12,0,$\bar{8}$ | 61 | +57 | 032 | 148 | +147 |
| 400 | 279 | −254 | 4,0,11 | < 11 | +11 | 12,0,$\bar{7}$ | 100 | +103 | 033 | 63 | +45 |
| 600 | < 9 | −36 | 4,0,12 | 34 | +55 | 12,0,$\bar{6}$ | 32 | −34 | 034 | < 15 | +21 |
| 800 | 84 | −88 | 6,0,$\overline{11}$ | < 11 | +13 | 12,0,$\bar{5}$ | 77 | +70 | 035 | 180 | +174 |
| 10,0,0 | 70 | −58 | 6,0,$\overline{10}$ | < 11 | −4 | 12,0 $\bar{4}$ | < 11 | +10 | 036 | < 17 | −25 |
| 12,0,0 | 132 | +156 | 60$\bar{9}$ | 32 | +36 | 12 0,$\bar{3}$ | 32 | −21 | 037 | 25 | +45 |
| 14,0,0 | 45 | −34 | 60$\bar{8}$ | 70 | −86 | 12,0,$\bar{2}$ | < 11 | +39 | 038 | 82 | +76 |
| 16,0,0 | 123 | −137 | 60$\bar{7}$ | 95 | +109 | 12,0,$\bar{1}$ | 45 | −52 | 039 | < 19 | −29 |
| 001 | < 5 | +18 | 60$\bar{6}$ | 100 | +104 | 12,0,1 | 89 | +75 | 0,3,10 | < 19 | +10 |
| 002 | 234 | −196 | 60$\bar{5}$ | 27 | +24 | 12,0,2 | 45 | −46 | 0,3,11 | < 19 | −12 |
| 003 | < 7 | −15 | 60$\bar{4}$ | 286 | −285 | 12,0,3 | 134 | −167 | 041 | 178 | −157 |
| 004 | 91 | −85 | 60$\bar{3}$ | 372 | −336 | 12,0,4 | 41 | −73 | 042 | 64 | −42 |
| 005 | 70 | +75 | 60$\bar{2}$ | 107 | +124 | 12,0,5 | < 11 | +36 | 043 | 192 | +180 |
| 006 | < 9 | −7 | 60$\bar{1}$ | < 9 | +3 | 12,0,6 | 16 | −24 | 044 | 55 | −55 |
| 007 | < 11 | −5 | 601 | < 9 | +2 | 12,0,7 | < 11 | −1 | 045 | < 17 | −7 |
| 008 | 30 | +59 | 602 | 98 | +80 | 14,0,$\bar{7}$ | < 9 | +11 | 046 | 25 | +37 |
| 009 | 16 | +24 | 603 | 161 | −142 | 14,0,$\bar{6}$ | < 11 | −4 | 047 | 80 | −88 |
| 0,0,10 | 170 | −215 | 604 | 61 | −73 | 14,0,$\bar{5}$ | 41 | +57 | 048 | 27 | +28 |
| 0,0,11 | 32 | −61 | 605 | 89 | −93 | 14,0,$\bar{4}$ | 41 | +65 | 049 | < 19 | +31 |
| 0,0,12 | < 9 | +32 | 606 | 134 | +137 | 14,0,$\bar{3}$ | 127 | −148 | 0,4,10 | < 19 | +5 |
| 2,0,$\overline{12}$ | 41 | −69 | 607 | 302 | +330 | 14,0,$\bar{2}$ | < 11 | −8 | 051 | 125 | −97 |
| 2,0,$\overline{11}$ | < 11 | −14 | 608 | 70 | −84 | 14,0,$\bar{1}$ | 32 | +46 | 052 | 156 | −134 |
| 2,0,$\overline{10}$ | < 11 | +1 | 609 | < 11 | −23 | 14,0,1 | 16 | −25 | 053 | 114 | +96 |
| 20$\bar{9}$ | < 11 | +32 | 6,0,10 | 16 | +19 | 14,0,2 | 91 | −108 | 054 | 59 | +41 |
| 20$\bar{8}$ | 23 | +30 | 8,0,$\overline{11}$ | 50 | +62 | 14,0,3 | < 11 | +32 | 055 | 93 | +110 |
| 20$\bar{7}$ | 116 | −136 | 8,0,$\overline{10}$ | 70 | −88 | 14,0,4 | < 11 | +15 | 056 | 97 | +94 |
| 20$\bar{6}$ | 148 | +175 | 80$\bar{9}$ | 54 | −75 | 14,0,5 | < 11 | −28 | 057 | < 19 | −5 |
| 20$\bar{5}$ | 157 | +169 | 80$\bar{8}$ | < 11 | +25 | 14,0,6 | 30 | −51 | 058 | 27 | −25 |
| 20$\bar{4}$ | < 9 | +3 | 80$\bar{7}$ | < 11 | −10 | 16,0,$\bar{5}$ | < 9 | −20 | 059 | < 19 | −32 |
| 20$\bar{3}$ | 34 | +36 | 80$\bar{6}$ | < 11 | +8 | 16,0,$\bar{4}$ | < 9 | +15 | 0,5,10 | < 19 | −27 |
| 20$\bar{2}$ | 304 | +309 | 80$\bar{5}$ | 166 | −203 | 16,0,$\bar{3}$ | < 11 | +7 | 061 | < 17 | −21 |
| 20$\bar{1}$ | 57 | −54 | 80$\bar{4}$ | < 9 | +7 | 16,0,$\bar{2}$ | < 11 | −10 | 062 | 25 | +11 |
| 201 | 73 | −63 | 80$\bar{3}$ | 27 | +38 | 16,0,$\bar{1}$ | 16 | +14 | 063 | 171 | −144 |
| 202 | 311 | −281 | 80$\bar{2}$ | 27 | +16 | 16,0,1 | 30 | −30 | 064 | 176 | −131 |
| 203 | 429 | +426 | 80$\bar{1}$ | 107 | −96 | 16,0,2 | 30 | +50 | 065 | 27 | −34 |
| 204 | 102 | −99 | 801 | 213 | +224 | 16,0,3 | < 9 | +8 | 066 | 129 | +107 |
| 205 | 225 | −214 | 802 | 54 | +60 | 16,0,4 | 36 | +56 | 067 | 131 | +146 |
| 206 | < 9 | −21 | 803 | < 9 | −7 | 020 | 237 | −208 | 068 | 27 | −45 |
| 207 | 129 | −138 | 804 | 91 | +62 | 040 | 25 | +18 | 069 | 27 | +25 |
| 208 | 75 | −74 | 805 | 170 | +166 | 060 | < 17 | +24 | 071 | 80 | +42 |
| 209 | < 11 | +11 | 806 | 32 | −39 | 080 | < 19 | −43 | 072 | 178 | +193 |
| 2,0,10 | < 11 | +33 | 807 | < 11 | −18 | 0,10,0 | < 17 | +9 | 073 | 104 | −106 |
| 2,0,11 | < 11 | +18 | 808 | < 11 | −26 | 011 | 32 | +27 | 074 | 64 | −64 |
| 2,0,12 | 27 | +47 | 809 | < 11 | −11 | 012 | 193 | +180 | 075 | < 19 | −7 |
| 4,0,$\overline{12}$ | < 9 | +23 | 8,0,10 | 73 | +108 | 013 | 247 | +228 | 076 | < 19 | −37 |
| 4,0,$\overline{11}$ | < 11 | +18 | 10,0,$\overline{10}$ | < 9 | +17 | 014 | 76 | +71 | 077 | 46 | −48 |
| 4,0,$\overline{10}$ | 102 | +120 | 10,0,$\bar{9}$ | < 11 | −24 | 015 | 332 | −339 | 078 | 27 | +48 |
| 40$\bar{9}$ | 32 | +44 | 10,0,$\bar{8}$ | 32 | +31 | 016 | 55 | +35 | 081 | 38 | −45 |
| 40$\bar{8}$ | 68 | +65 | 10,0,$\bar{7}$ | 116 | −135 | 017 | 76 | +89 | 082 | 64 | −66 |
| 40$\bar{7}$ | 59 | −70 | 10,0,$\bar{6}$ | 109 | −97 | 018 | 82 | +99 | 083 | 64 | +68 |
| 40$\bar{6}$ | 89 | −90 | 10,0,$\bar{5}$ | 54 | +74 | 019 | 64 | +58 | 084 | 27 | +10 |
| 40$\bar{5}$ | 157 | +170 | 10,0,$\bar{4}$ | 30 | +37 | 0,1,10 | 66 | −77 | 085 | < 19 | +1 |
| 40$\bar{4}$ | 25 | +34 | 10,0,$\bar{3}$ | 188 | +181 | 0,1,11 | < 19 | +34 | 086 | < 19 | +6 |
| 40$\bar{3}$ | 141 | +141 | 10,0,$\bar{2}$ | 52 | +25 | 021 | 78 | +76 | 087 | 72 | −67 |
| 40$\bar{2}$ | 20 | +14 | 10,0,$\bar{1}$ | 20 | +41 | 022 | 64 | +65 | 088 | 59 | +48 |
| 40$\bar{1}$ | 132 | −146 | 10,0,$\bar{1}$ | < 11 | −1 | 023 | 159 | +161 | 091 | < 19 | +3 |
| 401 | 43 | −47 | 10,0,$\bar{2}$ | 52 | +88 | 024 | 68 | +67 | 092 | < 19 | −33 |
| 402 | 316 | −252 | 10,0,3 | 30 | +41 | 025 | 85 | −87 | 093 | < 19 | −7 |
| 403 | < 9 | +22 | 10,0,4 | 98 | +103 | 026 | 57 | +55 | 094 | 27 | −65 |
| 404 | 220 | +220 | 10,0,5 | < 11 | −12 | 027 | 78 | −83 | 095 | < 19 | +15 |
| 405 | 284 | −269 | 10,0,6 | 45 | −50 | 028 | 82 | −98 | 096 | < 17 | −12 |
| 406 | 50 | +27 | 10,0,7 | 73 | −72 | 029 | < 19 | +20 | 0,10,1 | < 19 | −5 |
| 407 | < 11 | −21 | 10,0,8 | < 11 | −5 | 0,2,10 | 27 | +46 | 0,10,2 | < 17 | −11 |
| 408 | 32 | −22 | 10,0,9 | 50 | −49 | 0,2,11 | < 17 | −29 | 0,10,3 | < 17 | 0 |
| 409 | 64 | +80 | 12,0,$\bar{9}$ | 27 | −42 | 031 | 61 | −77 | 0,10,4 | 25 | +55 |

to any other position in the chain, charges of similar polarity would occur on two adjacent atoms.

When the intermolecular distances are investigated it is found that there are several extremely short distances which provide an answer to the question of stability. They are illustrated in the *b*-axis projection of Fig. 1 (*b*). The shortest distance of 2·85 Å occurs between atom 4 of one molecule and atom 4 of a neighboring molecule. Each molecule has two distances of 2·86 Å, one from atom 4 to atom 6 of a neighboring molecule, the other from atom 6 to atom 4 of a neighboring molecule. These two short distances do not occur in pairs to form a closed ring, but are related by a screw axis and spiral through the structure. The next shortest distance occurs at 3·20 Å between two number 8 atoms. There are also two distances of 3·35 Å between number 3 and number 4 atoms. All other distances are greater than or equal to 3·53 Å and are of no interest to the present discussion.

Pauling's equation relating bond distance and bond number (Pauling, 1947) was applied to the above data. The relation is

$$R(1)-R(n) = 0\cdot3 \log n\,, \qquad (2)$$

where $n$ is the bond number or number of electron pairs in a bond; $R(1)$ is the single bond radius and $R(n)$ is the radius of a bond of bond number $n$. Using a value of $R(1) = 1\cdot17$ Å for selenium, the following bond numbers were computed:

$$\begin{array}{ll}
n_{12} = 1\cdot65 & n_{81} = 0\cdot07 \\
n_{23} = 0\cdot93 & n_{44'} = 0\cdot14 \\
n_{34} = 1\cdot12 & n_{46'} = 0\cdot14 \\
n_{45} = 0\cdot86 & n_{64'} = 0\cdot14 \\
n_{56} = 1\cdot00 & n_{88'} = 0\cdot04 \\
n_{67} = 1\cdot17 & n_{34'} = 0\cdot02 \\
n_{78} = 0\cdot74 & n_{43'} = 0\cdot02
\end{array}$$

where a primed subscript indicates an atom in a neighboring molecule. The sum of the bond numbers for bonding within the chain is 7·47, while the sum per molecule for bonding external to the chain is 0·32. There are actually 8 electron pairs per molecule and equation (2) has accounted for 7·79 pairs. The missing 0·21 of an electron pair is almost certainly involved in bonds within the chain and can be accounted for by relatively small errors in the intramolecular bond distances. This is because of the logarithmic variation of $n$ in (2). For example, a decrease in $d_{12}$ of 0·03 Å would increase $n_{12}$ by 0·21, while an impossible decrease in $d_{34'}$ of 0·63 Å would be required to increase $n_{34'}$ by 0·21. Thus (2) indicates that approximately 7·7 electron pairs are used for bonding within each molecule while 0·3 of an electron pair per molecule is used for intermolecular bonding. The computed distribution of bonds is illustrated in Fig. 5, where the neighboring molecules around a given molecule are indicated schematically. The numbers between pairs of atoms indicate the number of electron pairs associated with each bond, while the numbers in parentheses indicate the number of valence electrons associated with each atom.

We conclude that β-selenium acquires sufficient stability to exist by virtue of being an electron-deficient compound. Of the sixteen valence electrons per molecule, about 0·6 of an electron is occupied in bonding external to the chain. Presumably the electron system then has sufficient mobility so that the bonding is somewhat metallic in character. However, the directional properties of the bonds within the chain are still predominantly covalent. The polarity of the atoms along the chain presents a sequence of some regularity that, again, is intermediate between the metallic and covalent extremes. An uncharged atom has two valence electrons associated with it. A larger or smaller number of valence electrons can be taken as a measure of the magnitude of the charge on an atom. In the case of a single covalent form of the molecule all the atoms are uncharged except numbers 2 and 8. In the present case the charges are redistributed all along the chain as indicated in Fig. 5. In addition to atom 2, atoms 4 and 6 have a considerable excess of valence electrons associated with them. The net result is a pattern of varying polarity that persists in a curious fashion from one end of the chain to the other.

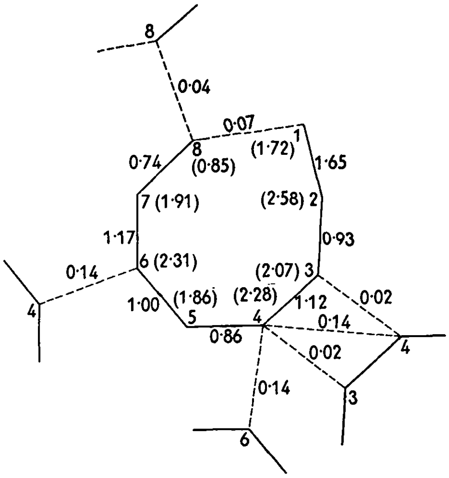

Fig. 5. Calculated bond numbers for β-selenium molecule. Positions of atoms in neighboring molecules indicated schematically. Numbers in parentheses are the number of valence electrons associated with each atom.

The more or less topographical description of the structure which has preceded would appear to be all that the present analysis by two-dimensional Fourier syntheses would justify. Indeed, one may well question whether all the variations in bond distances noted above are significant. The experimental data used on α- and β-selenium are strictly comparable. It was possible to average eight independent determinations of the selenium single-bond length in α-selenium and an average deviation of ±0·02 Å was found. The maximum deviation of any single determination from the average was ±0·03 Å. On this basis the distances reported for β-selenium should be reliable to ±0·03 Å. The function $_2R_2 = \Sigma(|F_o|-|F_c|)^2 \div \Sigma|F_o|^2$ was evaluated for the *h0l* and *0kl* reflections and yielded values of 0·0227 and 0·0328, respectively. According to Booth's interpretation of the function (Booth, 1948), the errors in the *b*-axis projection are zero, while in the *a*-axis projection the atomic co-ordinates have a root-mean-square error of 0·02 Å. Therefore, the estimate of accuracy of bond distances is probably reasonable. A fluctuation of ±0·03 Å could cancel much of the variation in bond distances along the chain molecule, yielding a sequence such as 2·24, 2·34, 2·34, 2·35, 2·34, 2·33 and 2·39 Å. The correlation of bond numbers by equation (2) would lead one to believe that the variations in bond distances are real, but to demonstrate it from X-ray evidence alone would call for an analysis by three-dimensional Fourier syntheses.

## The transition of β-selenium to metallic selenium

When X-ray photographs were taken of β-selenium crystals which had been preserved for a year under ordinary laboratory conditions a surprising detail was noted. In addition to the reflections of β-selenium, a second set of somewhat diffuse reflections was present on most of the photographs, the effect being most remarkable on the Weissenberg patterns obtained by rotation around the *c* axis. Fig. 7 illustrates the complete set of levels obtained by *c*-axis rotation using Cu *Kα* radiation. The zero, second and fourth levels include the normal reflections to be expected of β-selenium and also a second set of reflections which fall on a hexagonal lattice. On the zero level the hexagonal 0*k*.0 reflections fall along the same row as the monoclinic 0*k*0 reflections. The first, third and fifth levels contain only normal reflections.

The *hk*0 levels of the monoclinic and hexagonal reciprocal lattices are illustrated in Fig. 6. Certain of the monoclinic reflections which have been indexed fall almost exactly on the hexagonal lattice. The *c* axes of the direct lattices are exactly parallel and in the lower part of the figure the unit cells are projected along this axis. The following relations hold approximately:

$$\begin{aligned} a_{\text{monoclinic}} &= 3a_{\text{hexagonal}} \\ b_{\text{monoclinic}} &= (\sqrt{3})a_{\text{hexagonal}} \\ c_{\text{monoclinic}} &= 2c_{\text{hexagonal}} \;. \end{aligned}$$

The cell constants of metallic selenium just fit the observations on the hexagonal lattice.

We conclude that a single crystal of β-selenium can transform directly into a single crystal of metallic selenium. The β-selenium structure seems ready-made for such a transition and the general outlines of how it might occur are illustrated in the *b*-axis projection of Fig. 8. Vertical reference lines which are parallel to the *c*-axis divide the drawing into four sections which, reading from left to right, will be called the first, second, third and fourth sections of the figure. In the first section a group of nine β-molecules has been included so that the representation of the transformation can be carried along an integral number of eight hexagonal *c*-axis lengths. The covalent bonds of bond number 0·14 which occur between atoms 4 and 6 of one molecule and atoms 6 and 4 of two adjoining molecules are represented by broken lines. Atoms of the type marked 6′, 7′ and 8′ belong to molecules lying one *b*-axis translation above the other molecules in the figure. The transition is probably initiated by a great increase in bond number of the intermolecular bonds of bond number 0·14. Other bonds within the β molecules will be drained of electrons and the nature of the molecules will be altered drastically. It is then assumed that double-bonded atoms 1 and 2 will be quite reactive and that a new bond will be formed between atom 1 of one molecule and atom 1 of a neighboring molecule. Thus it is postulated that a β molecule disintegrates into four fragments: atoms 8–7–6, atom 5, atoms 4–3 and atoms 2–1. Simultaneously, new chain fragments are being formed with adjoining molecules of the types 8–7–6–4–3, 3–4–6′–7′–8′ and 2–1–1–2. The second section of Fig. 8 shows these new chain fragments arrayed along the direction of the *c*-axis. Each type of fragment is in a favorable configuration to link up with similar fragments to form indefinitely long chains. As the long chains are built up it is presumed that atoms of type 5 join the fragments at strategic points such that each chain accumulates atoms at the same

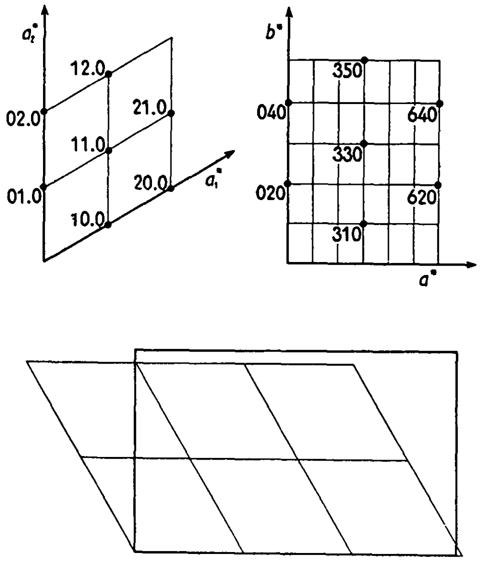

Fig. 6. Above: *hk*0 levels of monoclinic and hexagonal reciprocal lattices. Below: monoclinic and hexagonal unit cells projected along *c*-axis.

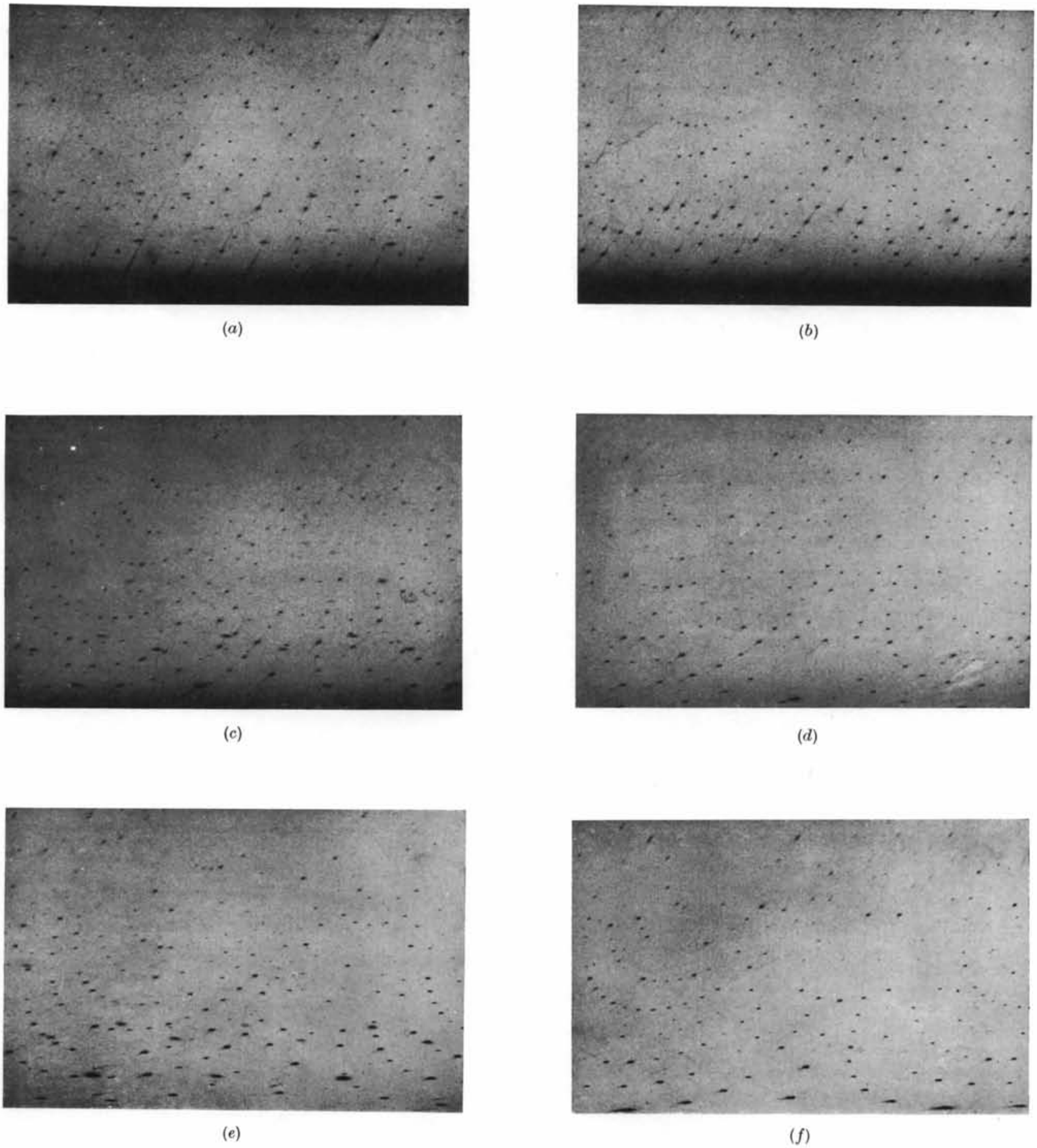

Fig. 7. Weissenberg patterns obtained by $c$-axis rotation of $\beta$-selenium crystal which has partly transformed into crystal of metallic selenium.

| | |
|---|---|
| (*a*) Zero level. | (*b*) First level. |
| (*c*) Second level. | (*d*) Third level. |
| (*e*) Fourth level. | (*f*) Fifth level. |

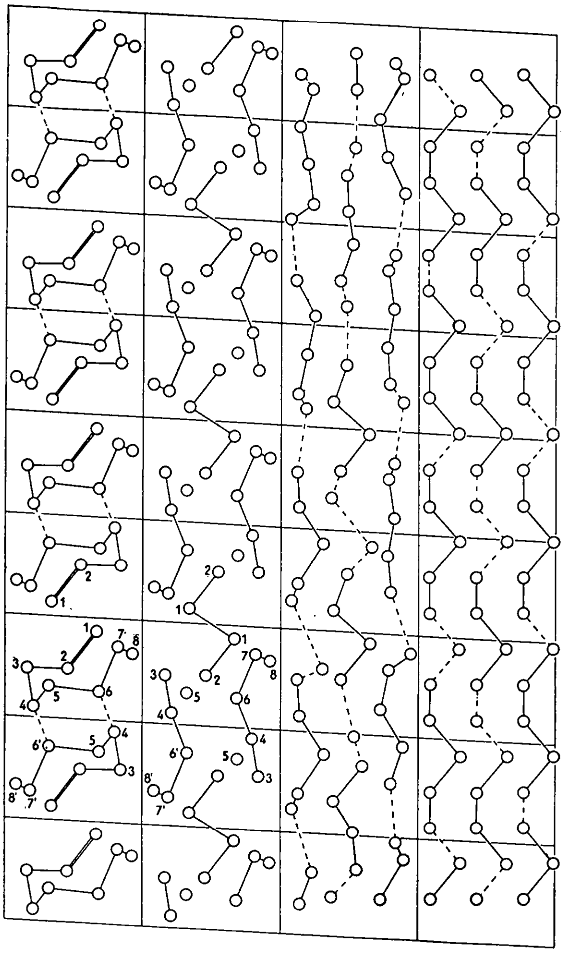

Fig. 8. Two-dimensional representation of transition from $\beta$-selenium to metallic selenium projected along the $b$-axis.

rate as its neighbors. In the third section of Fig. 8 chains of indefinite length are represented with atoms in a configuration intermediate between the initial and final states of the transformation. The four- and five-membered fragments of the second section of the figure can be identified by solid lines connecting the atoms. Bonds between fragments, between a fragment and a number 5 atom or between two number 5 atoms, are indicated by broken lines. Considerable reorientation is still necessary within each chain to reach the threefold helical configuration of metallic selenium, which is drawn in the fourth section of Fig. 8. However, this last step should occur quite easily because of the great stability of the metallic structure which arises from the four close contacts that each atom makes with atoms in neighboring chains.

## Discussion

The structure of $\beta$-selenium gives some indication of why many workers have doubted the existence of a second monoclinic polymorph. The conditions under which $\beta$-crystals can be grown are quite critical and not well understood. Of the various investigators who have reported on selenium in the literature, only Muthmann (1890) and Klug (1934) have prepared $\beta$ crystals. Muthmann stated that $\beta$ crystals were obtained by evaporation of cold, saturated solutions of selenium in carbon disulfide. In duplicating Muthmann's results the writer came to realize that the cold solution also had to be evaporated at a relatively rapid rate. A fourfold reduction in the volume of the solution over a 72 hr. period was used in the present research. It is likely that when crystal growth is conducted more slowly, the $\beta$ molecules have the opportunity to go back into solution and transform into $\alpha$ molecules. Kyropoulos (1927) and Halla, Bosch & Mehl (1931) let crystal growth occur over a period of several months and obtained only $\alpha$ crystals. Klug reported obtaining a solitary $\beta$ crystal plus many metallic crystals by a 70 hr. evaporation at 75° C. In this case it is likely that if other $\beta$ crystals were initially present they were transformed into metallic selenium by the temperature conditions.

Muthmann observed the formation of mixed crystals of orthorhombic sulfur and up to 35 atom% of selenium. No mixed crystals were formed between monoclinic sulfur and selenium. Also $\alpha$-selenium formed mixed crystals with up to 33 atom% of sulfur but $\beta$-selenium did not form mixed crystals. Both orthorhombic sulfur and $\alpha$-selenium contain ring molecules, and these molecular species are involved in the two cases cited of mixed-crystal formation. It is clear that the chain molecules of $\beta$-selenium would not form mixed crystals with sulfur ring molecules. The structure of monoclinic sulfur was examined by Burwell (1937) in terms of ring molecules but was not solved. The absence of mixed crystals between monoclinic sulfur and selenium ring molecules probably indicates that monoclinic sulfur does not contain the ring molecule of orthorhombic sulfur.

There are practically no measured properties of $\beta$-selenium with which the present structure can be tested. However, the pronounced semi-metallic luster of the crystals would be expected from the mobility which the electrons have. The bond distance of 2·21 Å found at one end of the molecule is similar to the value of 2·19 ± 0·03 Å found by Maxwell & Mosely (1940) for diatomic selenium molecules in the vapor phase by electron diffraction.

Von Hippel (1948) has considered the relation between structure and conductivity in the $\mathrm{VI}_b$ group of elements and introduced the concept of a resonance between an insulating and a metallic structure. This implies that in metallic selenium there is a resonance between an insulating chain structure held together by van der Waals forces and a simple cubic metallic structure. De Boer (1948) has given additional reasons for believing that the forces between chains in metallic selenium are not of the simple van der Waals type but that metallic forces are involved. The structure of $\beta$-selenium, which can be considered a transitory state between the ring molecules of α-selenium and the chains of metallic selenium, offers unexpected, but direct, evidence of metallic forces operating within and between molecules. It seems very reasonable that similar forces can account for the many fascinating properties of metallic selenium.

It is now possible to give an over-all picture of the polymorphism of selenium in terms of the underlying atomic configurations. Metallic selenium is a stable structure in which three-fold helical chains of infinite length are held together by forces which have an appreciable metallic contribution. At 217° C. the forces between chains are overcome and metallic selenium melts to a liquid composed of tangled chains. If liquid selenium is slowly cooled the forces between chains are able to bring back the ordered metallic arrangement. However, if liquid selenium is rapidly quenched to room temperature the tangled chains are frozen into solid, vitreous selenium. If vitreous selenium is gradually heated the forces between chains again operate to produce the ordered metallic structure. The various phases of this crystallization process, with the optimum nucleation rate near 90° C. and rapid crystal growth at higher temperatures, have been studied recently by von Hippel & Bloom (1950).

The forces that occur between chains depend on the close proximity of molecules in the solid state. When vitreous selenium is dissolved in carbon disulfide these forces are destroyed and there is no way to stabilize the isolated chains. As a result, 8-membered ring molecules are formed which can exist without intermolecular interactions. The α-selenium structure results from the direct crystallization of these molecules. However, sufficient thermal energy is available in the solution so that the ring molecules are continually breaking open and closing again. If the solution is cool the solubility of selenium is lowered and crystallization occurs rapidly. Then it is possible for ring molecules which have broken open to come together and crystallize. They are stabilized in the β-monoclinic structure by the strong forces between molecules. However, if β crystals are left in solution over a long period, some of the molecules return to the solution, become closed rings and then crystallize as α crystals. Gradually the β crystals will be depleted until only α crystals remain. With either α or β crystals, a transformation to the metallic structure occurs, proceeding more rapidly as the temperature is raised. In the case of β-selenium a single-crystal to single-crystal transition can occur at room temperature, as previously outlined. With α crystals more thermal energy is necessary to initiate the transformation and no detailed description of the change from rings to chains is possible. One can only point out that the rings probably break at points where the intermolecular distances are observed to be near the 3·49 Å value that exists between the chains of metallic selenium.

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