# Refinement of the Crystal Structure of α-Monoclinic Se

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The crystal structure of α-Se has been refined by an anisotropic least-squares method, using single-crystal integrated X-ray intensity data collected by counter diffractometry and by integrating Weissenberg techniques. Space group is $P2_1/n$. Cell dimensions at 26°C are $a = 9\cdot054 \pm 0\cdot003$, $b = 9\cdot083 \pm 0\cdot005$, $c = 11\cdot601 \pm 0\cdot006$ Å and $\beta = 90\cdot81 \pm 0\cdot05°$. There are four molecules per unit cell, and the measured and calculated X-ray densities are 4·46 and 4·43 g.cm$^{-3}$ respectively. The residual reliability value, $R$, for observed reflections is 0·072. Atoms combine to form $Se_8$ molecules and are arranged in a crown, approximating symmetry $\bar{8}2m$. Average Se–Se bond length is 2·336 (6) Å, which is significantly shorter than the bond length 2·373 (5) Å previously found in trigonal Se. The average angle in α-Se is 105·7 (1·6)°, while in trigonal Se it is 103·1 (2)°. These values compare with an average Se–Se bond length of 2·335 (22) Å and an average angle of 105·3 (2·3)° reported for α-Se by Burbank (1951), who recorded intensities of three zones using film techniques. Several intermolecular distances in α-Se are significantly shorter than predicted from the magnitudes of the van der Waals radii. Thermal parameters and ellipsoids have been determined for each atom. A rigid-body calculation has been completed, giving vibrational and librational motions of the $Se_8$ molecule.

Selenium exists in several modifications: trigonal (Bradley, 1924; Cherin & Unger, 1967), two monoclinic (Burbank, 1951; Marsh, Pauling & McCullough, 1953), vitreous (Lark-Horowitz & Miller, 1937), and possibly cubic (Andriovskii & Nabitovich, 1960). Only the trigonal form is thermodynamically stable at room temperature and pressure.

The vitreous modification is of interest to this laboratory, because of its xerographic properties. This modification is a complex combination of atoms that form closed rings and chains of various lengths. It is believed (Kaplow, Rowe & Averbach, 1968) that the short-range ordering of the chains is very similar to that occurring in the trigonal form and that the rings are very much like those in the α- and β-monoclinic modifications. Therefore, we studied the crystalline forms in detail to learn more about the vitreous phase.

In this article we discuss our investigation of the crystal structure of α-Se. An investigation was reported previously by Burbank (1951), who used data from three zones only. However, the precision did not suffice for our purposes: variation among bond lengths was fairly large (standard deviation $\pm 0\cdot022$ Å) and the reliability value was about 20%. A more recent study was made by Cherin & Unger (1966), using film techniques. In this case, the coupling between scale and temperature factors could not be entirely eliminated during the least-squares refinement. One bond length was somewhat larger than the average. Consequently, we lacked confidence in the accuracy, although the precision was satisfactory. Thus, it was considered worthwhile to carry out a more precise, and presumably more accurate, structure determination using counter techniques.

## Experimental

Crystals of α- and β-Se were grown by evaporation from a saturated solution of Se in $CS_2$. Although both

phases were deep red, the polyhedra of α-Se could easily be distinguished from the rod-like β-Se crystals. The α-Se crystals were ground into spheroids and two were selected. Their radii were approximately 0·09 mm. The crystals were not perfect spheres and the absorption effect was appreciable (for Cu $K\alpha$, $\mu R = 3\cdot7$; for Mo $K\alpha$, $\mu R = 3\cdot1$). However, errors due to absorption were reduced by collecting full three-dimensional data using counter and film methods, two radiations [Cu $K\alpha$ ($\lambda = 1\cdot5418$ Å) and Mo $K\alpha$ ($\lambda = 0\cdot7107$ Å)], and two crystals. Results were averaged.

Integrated intensity data were collected on an automatic Picker 4-angle programmer, equipped with a graphite monochromator, scintillation counter, and pulse-height analyzer. Background was determined at each end of the diffraction peak. It was assumed that background variation was linear across a reflection. A reflection was considered observed if $I \geq 2\sigma(I)$ for at least half of its equivalent reflections. The film data used in this determination had been collected for a previous study (Cherin & Unger, 1966) using Cu $K\alpha$ (Ni filter) and Mo $K\alpha$ (Zr filter) radiations in conjunction with a Nonius integrating Weissenberg camera. The crystal was mounted about the $c$ axis. Intensity measurements of these films were made with a Nonius Mark II photometer. Film data were scaled by comparison with counter data. Powder-diffraction data were collected with Cu $K\alpha$ radiation on a Philips diffractometer equipped with an LiF monochromator. Scanning speed was 0·25°/min; divergence slit was 0·5°; preslit was 1°, and the scatter slit was 0·5°.

## Crystal data and structure refinement

The space group of α-Se is $P2_1/n$. Lattice parameters were refined using the powder-diffractometry data and the least-squares program of Cherin, Lind & Davis (1970). Unit-cell dimensions are $a = 9\cdot054 \pm 0\cdot003$, $b =$

$9.083 \pm 0.005$, $c = 11.601 \pm 0.006$ Å, and $\beta = 90.81 \pm 0.05°$ Experimental density is 4.46 g.cm$^{-3}$ (Moss, 1952) and calculated density is 4.43 g.cm$^{-3}$. The number of molecules in the unit cell is four.

Measured intensities were corrected for Lorentz and polarization effects. A spherical absorption correction was applied. Anomalous dispersion corrections were required. For a unit cell containing only one kind of atom:

$$|F_{cor}| = |F_o|/[(1 + \delta_1)^2 + \delta_2^2]^{\frac{1}{2}},$$

where

$$\delta_1 = \Delta f'/f_o, \quad \delta_2 = \Delta f''/f_o .$$

Values of $\Delta f'$ and $\Delta f''$ were taken from Cromer (1965) and values of $f_o$ were taken from Cromer & Waber (1964). After these corrections, it was possible to correlate the Cu $K\alpha$ and Mo $K\alpha$ data. Film data were empirically scaled to the counter data. The $|F_o|$ were then compiled and averaged. Average deviation among the $|F_o|$ was 6%.

A full-matrix least-squares refinement (Busing, Martin & Levy, 1962) began with initial parameters taken from Cherin & Unger (1966). The function minimized was $\sum w_i[|F_{cor}| - (1/k)|F_c|)]^2$, where $w_i = [1/\sigma_i(F_{cor})]^2$. The standard deviation was taken from the statistical deviation determined when compiling equivalent reflections. However, the minimum standard deviation permitted was based on counting statistics. Data were refined, using the integrated intensity of 1108 reflections out of a possible 2529 within a reciprocal sphere of radius $\sin \theta/\lambda = 1.2$ Å$^{-1}$. Anisotropic temperature factors used had the form:

$$\exp [-(h^2 B_{11} + k^2 B_{22} + l^2 B_{33}$$
$$+ 2hl B_{13} + 2kl B_{23} + 2hk B_{12})] .$$

Convergence of the reliability value $R$ to 0.072 was achieved in three cycles. At this point, changes of temperature and position parameters were less than 1% of $\sigma(x)$. The reliability value was defined as:

$$R = \sum_n^N \frac{||F_{cor}| - |F_c||_n}{|F_{cor}|_n} ,$$

where $N$ is the total number of observed reflections. The standard deviation of an observation of unit weight is 1.46.

Results showed no evidence of extinction; thus, this correction was not applied. A listing of observed and calculated structure factors and standard deviations used are given in Table 1.

Bond lengths and angles, and lengths and orientation of the principal axes of the thermal ellipsoid, were calculated using ORFFE (Busing, Martin & Levy, 1964). A bond-length correction for rigid-body motion was calculated. This correction was based on the Cruickshank (1956) model in which we assumed that the center of libration is at the center of gravity.

## Description of the structure

In cubic Se (if it exists), it has been reported (Andriovskii & Nabitovich, 1960) that the atoms pack as 'hard spheres'. The bonding is presumably metallic in nature, as in Po. In trigonal Se the atoms bond covalently to form infinitely long chains which stack in a parallel manner. In the two monoclinic phases the selenium atoms form eight-membered crown-shaped rings. Intramolecular forces are covalent. The Se$_8$ molecules in α- and β-Se appear to be identical (Marsh et al., 1953). However, molecules pack differently in the two phases. The Se$_8$ molecule approximates $\bar{8}2m$ symmetry. Four atoms form a square on a plane, while the remaining four atoms lie on a nearly parallel plane. Two least-squares planes were determined. Coefficients are defined by $Ax + By + Cz = D$. Deviations (in Å) of atoms from the plane, distances between atoms on the plane, angles between these atoms, and the coefficients of the least-squares planes are given in Table 2. Small deviations from planarity do exist, and deviations appear to be systematic.

### Table 2. Deviations of atoms from least-squares planes

| Plane 1 | | Plane 2 | |
|---|---|---|---|
| Atom No. | Deviation Å | Atom No. | Deviation Å |
| 1 | −0.041 | 2 | 0.045 |
| 3 | 0.040 | 4 | −0.045 |
| 5 | −0.041 | 6 | 0.046 |
| 7 | 0.042 | 8 | −0.047 |

| Distances between atoms on planes | | | |
|---|---|---|---|
| 1–3 | 3.766 (6) Å | 2–4 | 3.781 (6) Å |
| 3–5 | 3.692 (5) | 4–6 | 3.751 (6) |
| 5–7 | 3.712 (5) | 6–8 | 3.677 (6) |
| 7–1 | 3.658 (5) | 8–2 | 3.740 (6) |

| Angles between atoms on planes | | | |
|---|---|---|---|
| 1–3–5 | 90.95 (6)° | 2–4–6 | 89.61 (5)° |
| 3–5–7 | 88.38 (6) | 4–6–8 | 90.06 (5) |
| 5–7–1 | 92.41 (6) | 6 8 2 | 91.49 (5) |
| 7–1–3 | 88.11 (6) | 8–2–4 | 88.68 (5) |

| Coefficients of planes | | | |
|---|---|---|---|
| $A = -0.1193$ | $C = 0.3866$ | $A' = -0.1334$ | $C' = 0.3763$ |
| $B = -0.9147$ | $D = 3.269$ | $B' = -0.9168$ | $D' = 4.495$ |

Atomic position parameters determined by least-square refinement are given in Table 3. Table 4 lists bond lengths and angles in the Se$_8$ molecule together with e.s.d.'s (in parentheses) as determined during the least-squares refinement. The correction for molecular motion was small, averaging 0.001 Å in bond length per atom. This correction is not included in the results in Table 4 because it was smaller than the e.s.d. Average bond length is 2.336 (6) Å and average bond angle is 105.7 (1.6)°. The standard deviation for the mean

Table 1. *Observed and calculated structure factors and* $\sigma(F_o)$

| h | k | l | 10Fo | 10Fc | 10σ |
|---|---|---|------|------|-----|

(Multi-column tabulation of observed and calculated structure factors. The columns repeat across the page with headings h, k, l, 10Fo, 10Fc, and 10σ.)

## Table 3. Fractional coordinates and vibration tensor components ($Å^2$)

E.s.d.'s are in parentheses. All values are $\times 10^4$.

| $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|
| 3209 (3) | 4840 (4) | 2362 (3) | 495 (16) | 468 (18) | 584 (18) | 111 (13) | −77 (13) | −19 (15) |
| 4254 (3) | 6625 (4) | 3569 (3) | 387 (14) | 508 (19) | 700 (20) | −101 (13) | −56 (13) | −41 (16) |
| 3178 (3) | 6376 (4) | 5378 (3) | 436 (14) | 497 (18) | 508 (18) | 22 (13) | −177 (13) | 30 (16) |
| 1343 (3) | 8186 (4) | 5529 (3) | 448 (14) | 455 (17) | 588 (19) | −32 (13) | −105 (13) | −16 (18) |
| −862 (3) | 6904 (4) | 5203 (3) | 400 (14) | 567 (19) | 453 (16) | −35 (13) | −1 (12) | 30 (18) |
| −1565 (3) | 7322 (4) | 3294 (3) | 341 (14) | 527 (19) | 576 (18) | 104 (13) | −100 (11) | 34 (18) |
| −814 (3) | 5217 (4) | 2290 (3) | 481 (16) | 402 (16) | 487 (16) | −88 (12) | −89 (12) | 29 (17) |
| 1301 (3) | 5990 (4) | 1337 (3) | 486 (16) | 463 (17) | 456 (16) | 26 (13) | −60 (13) | 1 (17) |

value was not calculated from the e.s.d.'s taken from the least-squares calculation, but from the deviations from the mean. As usual, this results in a larger standard deviation than predicted by the e.s.d.'s from the least-squares calculation. The bond angle is influenced by steric effects and intermolecular interactions. Thus, the fairly large standard deviation is probably due to physical factors rather than to statistical deviations. The average bond length compares well with 2·335 (22) Å found by Burbank (1951). Note, however, that there is a substantial improvement in precision. The average bond angle reported by Burbank (1951) is 105·3 (2·3)°. Other intramolecular distances are shown in Fig. 1.

### Table 4. Bond lengths and angles in the $Se_8$ molecule

| Atoms | | Atoms | |
|---|---|---|---|
| 1–2 | 2·333 (5) Å | 1–2–3 | 107·51 (4)° |
| 2–3 | 2·337 (5) | 2–3–4 | 107·68 (4) |
| 3–4 | 2·346 (5) | 3–4–5 | 104·08 (4) |
| 4–5 | 2·337 (4) | 4–5–6 | 107·10 (5) |
| 5–6 | 2·326 (4) | 5–6–7 | 105·23 (4) |
| 6–7 | 2·345 (5) | 6–7–8 | 103·65 (4) |
| 7–8 | 2·332 (4) | 7–8–1 | 103·97 (4) |
| 8–1 | 2·331 (5) | 8–1–2 | 106·60 (5) |
| Average value | 2·336 (6) | | 105·7 (1·6) |

The Se–Se bond length in α-Se is substantially shorter than that in trigonal Se, where it was reported as 2·373 (5) Å (Cherin & Unger, 1967). The difference in average bond length between the two phases can be related to the differences in intermolecular distances. In trigonal Se, each atom has four neighbors on adjacent molecules at a distance of 3·44 Å. In α-Se, intermolecular distances tend to be longer. A compilation of short intermolecular distances around the $Se_8$ molecule is given in Table 5. Atoms are marked with Roman numerals according to the molecule to which they belong (see Fig. 2). Table 5 shows that although several intermolecular distances in α-Se approach the 3·44 Å distance found in trigonal Se, most of them are much larger. Undoubtedly, the closer approach of 'nonbonded' atoms in trigonal Se results in a reduction of electron density between the covalently bonded atoms, producing a lengthened bond.

### Table 5. Significantly short intermolecular distances

| Atom No. | Atom No. | |
|---|---|---|
| 1[I] | 4[I] | 3·70 Å |
| 2[I] | 7[VI] | 3·70 |
| 3[I] | 6[IV] | 3·59 |
| 4[I] | 7[IV] | 3·57 |
| 5[I] | 8[V] | 3·48 |
| 6[I] | 3[V] | 3·59 |
| 6[I] | 7[VII] | 3·60 |
| 7[I] | 4[V] | 3·59 |
| 8[I] | 5[IV] | 3·48 |

In either case, intermolecular distances are significantly less than the predicted van der Waals distance of 4·0 Å (Pauling, 1940). Thus, interaction between the molecules in each case can not be accounted for by simple van der Waals type $r^{-6}$ dispersion forces, which is to be expected; the relatively small optical band gap for these semiconductors, 1·8 eV for trigonal Se (Choyke & Patrick, 1957) and 2·3 eV for α-Se. (Caywood & Mead, 1969), suggests significant intermolecular interactions.

Fig. 2 shows the $Se_8$ molecules projected onto the $ab$ plane. Dotted lines connect some of the atoms that have relatively close molecular distances. It is significant that if lines are drawn connecting these closely approaching atoms, a chain-like arrangement emerges. α-Se transforms rapidly to the stable trigonal phase at temperatures above 80°C. A mechanism for this conversion is suggested by the chain-like arrangements shown in Fig. 2. However, it is also possible to draw
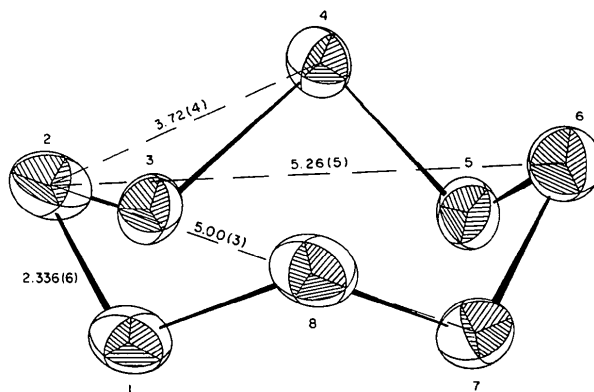


Fig. 1. Intramolecular distances and thermal ellipsoids of the $Se_8$ molecule. E.s.d.'s are in parentheses.
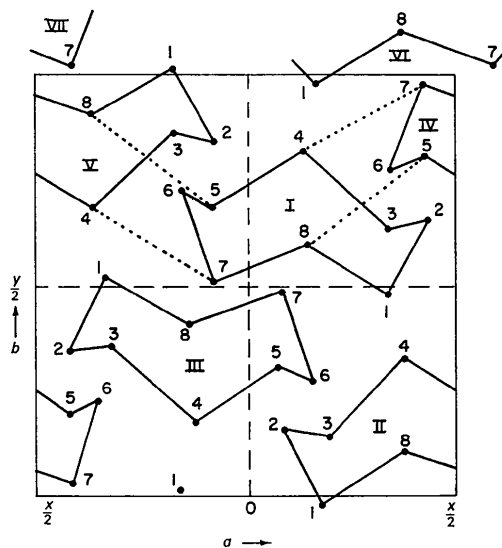
Fig. 2. Projection onto the *ab* plane.

a similar set of parallel chains perpendicular to those shown in Fig. 2. There is no evidence that one direction is preferable to the other. High-temperature studies would be useful to determine the preferred direction.

Table 6. *Rigid-body motion*

Principal axes

| R.m.s. amplitude | Direction cosines with respect to unit-cell axes | | |
|---|---|---|---|
| | *a* | *b* | *c* |
| 0·277 Å | 0·469 | 0·883 | 0·006 |
| 0·177 | −0·276 | 0·153 | −0·949 |
| 0·142 | −0·839 | 0·444 | 0·316 |

Libration motion

| | Direction cosines with respect to unit-cell axes | | |
|---|---|---|---|
| | *a* | *b* | *c* |
| 4·0° | 0·404 | −0·903 | −0·143 |
| 3·4 | 0·255 | 0·261 | −0·931 |
| 2·4 | 0·879 | 0·340 | 0·336 |

The thermal parameters are listed in Table 3 in terms of $U_{ij}$ (units of Å$^2$), where $U_{ij}$ is defined as $b_{ij}/2\pi^2 a_i^* a_j^*$. Thermal ellipsoids of $Se_8$ are shown in Fig. 1. Deviations from isotropic motion are not large. Results of a rigid-body calculation are given in Table 6. The root-mean-square amplitudes of the principal axes of translational vibration of the mass center are listed together with their direction cosines with respect to the unit-cell axes. Angular oscillations (r.m.s. amplitude) about axes through the center of the molecule are given in Table 6.

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