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Structure of the Pressure-Induced Phase of $S_{0.56}Se_{0.44}$

S. GELLER AND M. D. LIND

Science Center, North American Rockwell Corporation, Thousand Oaks, California 91360

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The structure of the pressure-induced phase of $S_{0.56}Se_{0.44}$ has been determined from "single"-crystal x-ray diffraction data estimated from Weissenberg photographs. Crystals of this phase belong to space groups $P3_1$ or $P3_2$ but are 60° rotation twinned and thus give diffraction symmetry $6/m$. The lattice constants are $a=7.85$, $c=4.62\pm 0.01$ Å; each unit cell contains five S and four Se atoms. The structure contains three crystallographically nonequivalent helical molecules of different composition, namely 60%, 67%, and 40% sulfur, with the average equal to 56% sulfur. Best agreement between calculated and observed structure amplitudes is obtained by allowing disorder in position of one specific molecule.

INTRODUCTION

In this paper, we report the results of a structure determination of the pressure-induced phase $S_{0.56}Se_{0.44}$, a solid solution with a structure different from those of any known form of either sulfur or selenium. The structures of the pressure-induced phases involving the

chalcogens have a number of interesting features which have, to some extent, already been discussed elsewhere.¹⁻⁵ These are associated with the helical nature of the molecules.

As shown previously,^{3,5} the $S_{0.56}Se_{0.44}$ crystals contain 3_1 or 3_2 helical molecules. The unit cell contains three three-atom helix segments. To account for the $6/m$

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diffraction symmetry observed³ for the crystals, twinning or disorder must be assumed. Structural models having the symmetry of one of the space groups $P3_1$, $P3_2$, $P6_1$, or $P6_5$ may be considered. In the case of $P3_1$ or $P3_2$, to account for the diffraction symmetry, either 60° rotational twinning or disorder of all the molecules must be assumed. In the case of $P6_1$ or $P6_5$, at least one of the three molecules per unit cell must be disordered.

Attempts to refine the structure led finally to a model having space group $P3_1$ or $P3_2$ with twinning; the three crystallographically different molecules have different composition and one of the molecules (II in Fig. 1) is disordered. Our results indicate that this molecule is probably disordered over four positions related by 30° turns about the 3_1 axis and translations of $\frac{1}{2}$ along this axis. Introduction of the disorder was required to obtain reasonable values for the temperature factors and the composition of molecule II. The anomalous nature of molecule II was manifested in initial least-squares refinement calculations which utilized only data with $l=0$, and persisted throughout the subsequent refinement calculations.

EXPERIMENTAL

An earlier publication³ describes the conditions of preparation of the $S_{0.56}Se_{0.44}$ and gives preliminary information on its structure. For the sake of completeness, we summarize the crystallographic data in Table I.

The intensity data were obtained from the multiple Weissenberg photographs taken about the c axis; Cu $K\alpha$ radiation was used. Intensities were estimated by comparison with a calibrated intensity scale. Lorentz-polarization factors were applied to the data. The linear absorption coefficient (Cu $K\alpha$ rad) for $S_{0.56}Se_{0.44}$ is 274 cm^{-1} ; the cross section of the crystal was approximately rectangular with dimensions $0.05 \times 0.07 \text{ mm}$.

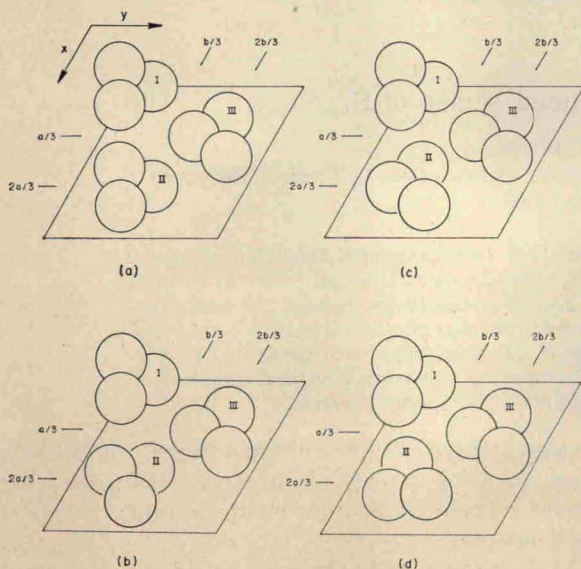


Fig. 1. Projections of the structure on (001); (a), (b), (c), and (d) show the four orientations of molecule II (see Table II).

TABLE I. Crystallographic data^a for $S_{0.56}Se_{0.44}$.

| |
|--|
| Most probable space group: $P3_1-C_3^2$ or $P3_2-C_3^2$ |
| Lattice constants: $a = 7.85 \pm 0.01$; $c = 4.62 \pm 0.01$ |
| Unit cell volume: 247 \AA^3 |
| Unit cell contains five S and four Se atoms (average) |
| Calculated density: 3.20 g cm^{-3} |
| Measured density: 3.20 g cm^{-3} |
| Systematic absences: $00l$ with $l \neq 3n$ |

^a From Ref. 3.

Absorption corrections⁶ were made assuming the crystal to be cylindrical with $r = 0.003 \text{ cm}$ ($\mu r = 0.8$). This approach seemed adequate, the error in the correction on the structure amplitudes being at worst about $\pm 3\%$.

REFINEMENT OF THE STRUCTURE

The asymmetric unit of the structure contains three atoms, one from each of the three molecular segments which are located at the three 3_1 or 3_2 axes of the unit cell. With one z coordinate fixed and the four positions of the disordered molecule tied together and described by a single set of variable coordinates, x , y , and z , there are eight variable positional parameters. There are three isotropic or 18 anisotropic thermal parameters. Trial values of the positional parameters were deduced from packing considerations carried out with scale models.

The Busing-Martin-Levy⁷ least-squares program was used for the refinement calculations. The function minimized was $\sum w(|F_0| - k^{-1}|F_c|)^2$, in which w is a weighting function (for $F_0 \geq 16$, $w = 100/|F_0|^2$; for $F_0 < 16$, $w = 0.39$) and k is a scale factor. Only $|F_0|$ above background were included in the least-squares calculations, although structure factors were calculated for all hkl in the range of the intensity measurements. To take the twinning into account, the least-squares program was modified so that structure amplitudes were calculated according to $|F_c| = (1/\sqrt{2})(|F_1|^2 + |F_2|^2)^{1/2}$ in which $|F_1|$ and $|F_2|$ are the structure amplitudes for two twins rotated 60° from each other. (If $|F_1|$ is $|F_{hkl}|$, $|F_2|$ is equivalent to $|F_{\bar{h}\bar{k}l}|$, where $-i = h+k$.) The scattering factors used were those given by Dawson⁸ for sulfur and those given by Freeman and Watson⁹ for selenium. In all calculations the real part of the dispersion correction¹⁰ was applied to both, and in the later calculations the imaginary part was applied. At first, weighted average scattering factors corresponding to an atom made up of $\frac{5}{9}$ S and $\frac{4}{9}$ Se were used. The scattering factor multipliers for the three independent atoms were allowed to vary in the least-squares calculations to allow for nonuniformity in their compositions. In later calculations both the sulfur and selenium scattering factors were used and the multipliers were used as variables to adjust the contribution of each in each of the three molecules. The multipliers, thermal parameters, and scale factors could not be allowed to vary simultaneously because of 1:1 pair correlations¹¹ among these parameters.

An initial series of least-squares calculations utilizing only data with $l=0$ was carried out because this allowed

TABLE II. Final values of positional and isotropic thermal parameters.^a

| Atom No. | %S | x | y | z | B (Å ²) |
|----------|----|-------|-------|--------|---------------------|
| 1 | 40 | 0.001 | 0.121 | 0.000 | 5.30 |
| 2 | 67 | 0.667 | 0.453 | -0.109 | 5.66 |
| | 67 | 0.597 | 0.403 | -0.026 | 5.66 |
| | 67 | 0.547 | 0.333 | 0.057 | 5.66 |
| | 67 | 0.528 | 0.264 | 0.141 | 5.66 |
| 3 | 60 | 0.460 | 0.780 | -0.171 | 5.59 |

^a Atom numbers 1, 2, 3 correspond to molecule numbers I, II, III. For atoms 2: Positions are taken according to the relation given in the text; only the first z parameter was permitted to vary. The z of atom 1 was fixed at 0.000. With the stated constraints, the final least-squares calculation gave σ 's of 0.001 for x and y parameters, 0.006-0.008 for z parameters, and 0.2-0.3 Å² for B parameters.

refinement of the trial x and y parameters for space group $P3_1$ without special treatment to account for the $6/m$ diffraction symmetry. After these calculations had converged, further series of calculations with the full set of data were carried out, first with isotropic thermal parameters and subsequently with anisotropic ones. The least-squares calculations were continued until all parameter changes were negligibly small and the discrepancy factor, $R = \sum ||F_0| - |F_c|| / \sum |F_0|$, had decreased to 0.11. However, throughout the calculations, the thermal parameters of molecule II, both when held isotropic and when allowed to be anisotropic, tended to be unreasonably high (of the order of $B = 9-12$ Å², as compared with $B = 4-6$ Å² for the other molecules), or when the thermal parameters of the three molecules were constrained to be equal, the multiplier for molecule II tended toward a high sulfur content (up to 90% S). Furthermore, the compositions of the three molecules were not satisfactorily consistent with the positional parameters. High correlations¹¹ between certain pairs of parameters were found throughout the calculations.

Additional least-squares calculations were made with several different trial values for the positional parameters of molecule II. None of these was found to lead to a better result than that obtained originally. However, from a series of least-squares calculations utilizing only the data with $l=0$ it was found that rotation of molecule II by 30° increments from the original position gave three new nonequivalent positions which were apparently no worse than the original one. Each led to temperature factors of $B = 9-12$ Å² for molecule II. This implied that molecule II might be disordered over at least these four positions. When this disorder was included in the least-squares calculations, without allowing the molecule II positions to vary, the isotropic temperature factor of molecule II refined to an apparently reasonable value only slightly higher than those of the other two molecules.

Further least-squares calculations showed that no further improvement was obtained with molecule II disordered over 16 positions corresponding to $7\frac{1}{2}^\circ$ increments of rotation from the original position. On the

other hand, it was found that disorder of the molecule over only two positions, namely, the original one and one rotated 60° from it, leads to results no better than those obtained without disorder. It was concluded that molecule II is probably disordered over four sets of positions. From considerations of the packing it appeared that the z coordinates of the three new positions are given very nearly by $z_0 + \frac{1}{12}$, $z_0 + \frac{1}{6}$, and $z_0 + \frac{1}{4}$, respectively, where z_0 is the value for the original position. With these values of z , least-squares calculations utilizing the full set of data, still without allowing the molecule II positions to vary, also yielded satisfactory isotropic temperature factor values.

After it had been established that the disordered model leads to an apparent improvement in the thermal parameters, the multipliers were readjusted by a trial-and-error method in which several least-squares calculations were made with various combinations of multiplier and thermal parameter values to find those which gave the best over-all and individual agreement between $|F_0|$ and $|F_c|$. Then, a final least-squares calculation, in which all three multipliers and the x and y for molecule II were held constant and the z 's for molecule II were constrained according to the relationship indicated above, was carried out. Because without drastic program changes it was not possible to use a single set of anisotropic thermal parameters for the disordered molecule II, all thermal parameters were kept isotropic. The final calculation yielded (with the constraints described above) the positional and isotropic thermal parameter values shown in Table II. Table III gives a comparison of the $|F_c|$ with the

TABLE III. Comparison of observed and calculated structure amplitudes. Note $|F_{hkl}| \equiv (1/\sqrt{2}) (|F_{hkl}|^2 + |F_{\bar{h}\bar{k}l}|^2)^{1/2}$, $-i = h+k$.

| $z = 0$ | | $z = 0(\text{cont'd})$ | | $z = 1(\text{cont'd})$ | | $z = 2(\text{cont'd})$ | | |
|---------|---------|------------------------|----|------------------------|---------|------------------------|---------|---------|
| hk | $ F_0 $ | $ F_c $ | hk | $ F_0 $ | $ F_c $ | hk | $ F_0 $ | $ F_c $ |
| 10 | 24 | 20 | 36 | 9 | 7 | 35 | 17 | 17 |
| 20 | 3 | 3 | 17 | 25 | 23 | 45 | 10 | 9 |
| 30 | 31 | 26 | 27 | <4 | 3 | 16 | <6 | 5 |
| 40 | 7 | 11 | 18 | 4 | 5 | 26 | 14 | 12 |
| 50 | 7 | 7 | | | | 36 | 12 | 10 |
| 60 | 7 | 10 | | | | 17 | 8 | 9 |
| 70 | 9 | 11 | | | | 27 | 5 | 6 |
| 80 | 8 | 7 | | | | 18 | <3 | 2 |
| 90 | 8 | 7 | hk | $ F_0 $ | $ F_c $ | | | |
| 10 | 11 | 11 | 10 | 20 | 17 | | | |
| 20 | 21 | 20 | 20 | 31 | 29 | | | |
| 30 | 31 | 30 | 30 | 41 | 39 | | | |
| 40 | 41 | 40 | 40 | 51 | 49 | | | |
| 50 | 51 | 50 | 50 | 61 | 59 | | | |
| 60 | 61 | 60 | 60 | 71 | 69 | | | |
| 70 | 71 | 70 | 70 | 81 | 79 | | | |
| 80 | 81 | 80 | 80 | 91 | 89 | | | |
| 90 | 91 | 90 | 90 | 101 | 99 | | | |
| 10 | 10 | 10 | 10 | 110 | 100 | | | |
| 20 | 20 | 20 | 20 | 120 | 110 | | | |
| 30 | 30 | 30 | 30 | 130 | 120 | | | |
| 40 | 40 | 40 | 40 | 140 | 130 | | | |
| 50 | 50 | 50 | 50 | 150 | 140 | | | |
| 60 | 60 | 60 | 60 | 160 | 150 | | | |
| 70 | 70 | 70 | 70 | 170 | 160 | | | |
| 80 | 80 | 80 | 80 | 180 | 170 | | | |
| 90 | 90 | 90 | 90 | 190 | 180 | | | |
| 10 | 10 | 10 | 10 | 200 | 190 | | | |
| 20 | 20 | 20 | 20 | 210 | 200 | | | |
| 30 | 30 | 30 | 30 | 220 | 210 | | | |
| 40 | 40 | 40 | 40 | 230 | 220 | | | |
| 50 | 50 | 50 | 50 | 240 | 230 | | | |
| 60 | 60 | 60 | 60 | 250 | 240 | | | |
| 70 | 70 | 70 | 70 | 260 | 250 | | | |
| 80 | 80 | 80 | 80 | 270 | 260 | | | |
| 90 | 90 | 90 | 90 | 280 | 270 | | | |
| 10 | 10 | 10 | 10 | 290 | 280 | | | |
| 20 | 20 | 20 | 20 | 300 | 290 | | | |
| 30 | 30 | 30 | 30 | 310 | 300 | | | |
| 40 | 40 | 40 | 40 | 320 | 310 | | | |
| 50 | 50 | 50 | 50 | 330 | 320 | | | |
| 60 | 60 | 60 | 60 | 340 | 330 | | | |
| 70 | 70 | 70 | 70 | 350 | 340 | | | |
| 80 | 80 | 80 | 80 | 360 | 350 | | | |
| 90 | 90 | 90 | 90 | 370 | 360 | | | |
| 10 | 10 | 10 | 10 | 380 | 370 | | | |
| 20 | 20 | 20 | 20 | 390 | 380 | | | |
| 30 | 30 | 30 | 30 | 400 | 390 | | | |
| 40 | 40 | 40 | 40 | 410 | 400 | | | |
| 50 | 50 | 50 | 50 | 420 | 410 | | | |
| 60 | 60 | 60 | 60 | 430 | 420 | | | |
| 70 | 70 | 70 | 70 | 440 | 430 | | | |
| 80 | 80 | 80 | 80 | 450 | 440 | | | |
| 90 | 90 | 90 | 90 | 460 | 450 | | | |
| 10 | 10 | 10 | 10 | 470 | 460 | | | |
| 20 | 20 | 20 | 20 | 480 | 470 | | | |
| 30 | 30 | 30 | 30 | 490 | 480 | | | |
| 40 | 40 | 40 | 40 | 500 | 490 | | | |
| 50 | 50 | 50 | 50 | 510 | 500 | | | |
| 60 | 60 | 60 | 60 | 520 | 510 | | | |
| 70 | 70 | 70 | 70 | 530 | 520 | | | |
| 80 | 80 | 80 | 80 | 540 | 530 | | | |
| 90 | 90 | 90 | 90 | 550 | 540 | | | |
| 10 | 10 | 10 | 10 | 560 | 550 | | | |
| 20 | 20 | 20 | 20 | 570 | 560 | | | |
| 30 | 30 | 30 | 30 | 580 | 570 | | | |
| 40 | 40 | 40 | 40 | 590 | 580 | | | |
| 50 | 50 | 50 | 50 | 600 | 590 | | | |
| 60 | 60 | 60 | 60 | 610 | 600 | | | |
| 70 | 70 | 70 | 70 | 620 | 610 | | | |
| 80 | 80 | 80 | 80 | 630 | 620 | | | |
| 90 | 90 | 90 | 90 | 640 | 630 | | | |
| 10 | 10 | 10 | 10 | 650 | 640 | | | |
| 20 | 20 | 20 | 20 | 660 | 650 | | | |
| 30 | 30 | 30 | 30 | 670 | 660 | | | |
| 40 | 40 | 40 | 40 | 680 | 670 | | | |
| 50 | 50 | 50 | 50 | 690 | 680 | | | |
| 60 | 60 | 60 | 60 | 700 | 690 | | | |
| 70 | 70 | 70 | 70 | 710 | 700 | | | |
| 80 | 80 | 80 | 80 | 720 | 710 | | | |
| 90 | 90 | 90 | 90 | 730 | 720 | | | |
| 10 | 10 | 10 | 10 | 740 | 730 | | | |
| 20 | 20 | 20 | 20 | 750 | 740 | | | |
| 30 | 30 | 30 | 30 | 760 | 750 | | | |
| 40 | 40 | 40 | 40 | 770 | 760 | | | |
| 50 | 50 | 50 | 50 | 780 | 770 | | | |
| 60 | 60 | 60 | 60 | 790 | 780 | | | |
| 70 | 70 | 70 | 70 | 800 | 790 | | | |
| 80 | 80 | 80 | 80 | 810 | 800 | | | |
| 90 | 90 | 90 | 90 | 820 | 810 | | | |
| 10 | 10 | 10 | 10 | 830 | 820 | | | |
| 20 | 20 | 20 | 20 | 840 | 830 | | | |
| 30 | 30 | 30 | 30 | 850 | 840 | | | |
| 40 | 40 | 40 | 40 | 860 | 850 | | | |
| 50 | 50 | 50 | 50 | 870 | 860 | | | |
| 60 | 60 | 60 | 60 | 880 | 870 | | | |
| 70 | 70 | 70 | 70 | 890 | 880 | | | |
| 80 | 80 | 80 | 80 | 900 | 890 | | | |
| 90 | 90 | 90 | 90 | 910 | 900 | | | |
| 10 | 10 | 10 | 10 | 920 | 910 | | | |
| 20 | 20 | 20 | 20 | 930 | 920 | | | |
| 30 | 30 | 30 | 30 | 940 | 930 | | | |
| 40 | 40 | 40 | 40 | 950 | 940 | | | |
| 50 | 50 | 50 | 50 | 960 | 950 | | | |
| 60 | 60 | 60 | 60 | 970 | 960 | | | |
| 70 | 70 | 70 | 70 | 980 | 970 | | | |
| 80 | 80 | 80 | 80 | 990 | 980 | | | |
| 90 | 90 | 90 | 90 | 1000 | 990 | | | |

^a Intensities too high to be satisfactorily estimated.

$|F_0|$ calculated from these parameter values. The final value of R is 0.11.

An alternate solution, namely replacement of molecule II by a pure sulfur helix with 10 atoms per three turns, was explored extensively but was finally rejected. In this model the lattice constant c is tripled and the symmetry is lowered to that of space group $P1$. To account for the $6/m$ diffraction symmetry, an effectively sextuply twinned crystal must be assumed. This model did not lead to satisfactory agreement between $|F_0|$ and $|F_c|$, especially for many of the unobserved data, including those of intermediate reciprocal lattice levels which should occur when c is tripled.

DISCUSSION

The attempt to refine the structure of the pressure-induced phase of $S_{0.56}Se_{0.44}$ suffered from a number of complications. These were: large correlations between parameters, rotation twinning, positional disorder, and insufficient data for the large number of variable parameters. Further, because of the gradual decomposition of the crystal by the x irradiation,⁵ to minimize exposure time, the photographic technique was used. From our experience with the structure of the pressure-induced fibrous sulfur phase, we believe it unlikely that significant improvement could have been attained in this case with counter data and attempts to replace crystals as they became too degraded by the exposure to x rays. Thus, as in the sulfur case,² we do not claim to have achieved an ultimately refined structure. We believe, however, that we have made the best of a complicated situation and that the structure proposed for this phase is essentially correct.

It is possible, and perhaps probable, that the disorder is more complicated than as given. One may well question why it is that only one of the three crystallographically nonequivalent molecules may have more than one position in the structure. It could be that other combinations of disorder would give equally good, or perhaps better, agreement between calculated and observed amplitudes and physically reasonable values for the composition and for the positional and thermal parameters. No attempt was made to explore this possibility; the number of possible combinations is very large and we have decided that further effort on this problem is unwarranted.

We were rather surprised to find that the compositions of the three molecules differed. However, forcing the molecules to have the same composition impairs the agreement between calculated and observed amplitudes and gives unreasonable values of thermal parameters. Thus we must conclude that for best packing in the solid state, the compositions of the nonequivalent molecules must be different. This implies that some intermolecular diffusion occurs during the crystallization process.

Interatomic distances and angles were calculated with the ORTEP program.¹² Within each molecule the nearest-neighbor distance is 2.25 Å. The S-S distance in fibrous sulfur is 2.07 Å; in hexagonal Se,¹³ the Se-Se distance is

2.32 Å. For a 40% S molecule, the calculated bond distance is 2.21 Å; for a 60% S molecule, it is 2.17, and for a 67% S molecule, it is 2.15 Å. At least the last two are substantially lower than the observed value.

The space group fixes the vertical distance between two nearest atoms in a molecule to $c/3$ or 1.54 Å (see Ref. 14); thus the variables on which the bond distance depends are x and y . In the least-squares calculations while the values of these parameters were fixed for the "disordered" molecule, they were allowed to vary for the two other molecules. Convergence under the imposed constraints led to the observed bond distance and to rather small σ^2 's (0.001) in the x and y parameters for these two molecules. If the standard errors are meaningful, then the difference between observed and "calculated" bond distance is significant for molecule III.

The helix radii are 0.95 ± 0.03 Å; in hexagonal Se¹³ it is 0.95 Å. The interbond angles in all three molecules are 102° ; it is 105° in hexagonal Se,¹³ 102° - 109° in α -Se,¹⁵ 104° - 107° in β -Se,¹⁶ 106° in pressure-induced fibrous S ($^{10}S_3$ helix),² 108° in orthorhombic¹⁷ S, and 102° in rhombohedral¹⁸ S.

The shortest distance between nonbonded atoms in all three molecules is 3.49 Å. The shortest distance between atoms in different molecules is 3.54 Å; in hexagonal Se, the closest approach between atoms in different chains is 3.46 Å. (The poorer packing efficiency of the pressure-induced $S_{0.56}Se_{0.44}$ phase than of hexagonal Se had been deduced earlier.³)

The dihedral angle formed by a sequence of four consecutive atoms, that is, between the planes of the first three and the last three is 100° . This angle is 95° in fibrous sulfur and 98° - 101° in orthorhombic sulfur. (These angles were not calculated in Refs. 13, 15, and 16.)

Projections of the structure down the c axis are shown in Fig. 1. The different projections show the different possible orientations of molecule II.

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