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

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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 $a=7.85$, $c=4.62\pm0.01$ 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 $6/m$

diffraction symmetry observed[3] 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 $\frac{1}{12}$ 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 publication[3] 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 0.05×0.07 mm.
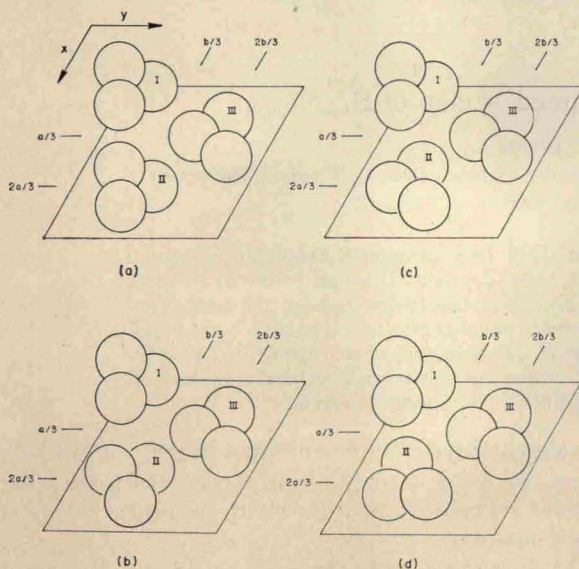

(a)   (c)

(b)   (d)

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_3^3
Lattice constants: $a=7.85\pm0.01$; $c=4.62\pm0.01$
Unit cell volume: 247 Å^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 $l\neq3n$

[a] From Ref. 3.

Absorption corrections[6] were made assuming the crystal to be cylindrical with $r=0.003$ cm ($\mu r=0.8$). This approach seemed adequate, the error in the correction on the structure amplitudes being at worst about $\pm3\%$.

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–Levy[7] 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 $F_0\geq16$, $w=100/|F_0|^2$; 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 $|F_{\bar{k}\bar{i}l}|$, where $-i=h+k$.) The scattering factors used were those given by Dawson[8] for sulfur and those given by Freeman and Watson[9] for selenium. In all calculations the real part of the dispersion correction[10] 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 $\frac{4}{9}$ S 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 correlations[11] among these parameters.

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