

also been prepared earlier; it seems that the powder lines reported for "white sulfur" designated ω by Das,¹⁵ who prepared it by hydrolysis of S_2Cl_2 (and further physical treatment), agree in spacing and relative intensity with the seven strongest lines of the powder photograph of our phase I (see Table 2 of Ref. 1).

SULFUR-SELENIUM

The pressure-induced sulfur-selenium phase was made² at 20 kb after holding at 550°C for 10 min and annealing for 56 hr at 280°C. The phase has a solid solution range, the extent of which we have not determined. The crystals are red-brown. The particular composition of the crystal on which we have done structural studies is close to $S_{0.56}Se_{0.44}$. We write the formula in this manner to indicate that although this phase is not isostructural with any sulfur or any selenium phase, it is nevertheless a solid solution phase, not a compound and not, as in the case of Te_7S_{10} (see below), a cocrystallization of atomically pure dissimilar helical molecules.

Weissenberg and Buerger precession camera photographs were taken of a crystal of the new phase. The diffraction symmetry is $6/m$; $00l$ reflections are present only

when $l = 6n$. The lattice constants of the crystal studied are $a = 7.85 \pm 0.01$, $c = 4.62 \pm 0.01$ Å. Five sulfur and four selenium atoms per unit cell give a calculated density equal to the measured value, 3.20 g cm^{-3} . The relation of the unit cell to that of hexagonal selenium indicated the probable presence of helical molecules with an average of three atoms per turn.

Excluding disorder, hexagonal space groups giving diffraction symmetry $6/m$ cannot satisfy the requirements for this structure. Thus it appears that the $6/m$ may be only an apparent diffraction symmetry; the more probable diffraction symmetry is $\bar{3}$. When crystals with this symmetry are 60° rotation-twinned, they give the apparent symmetry observed. This is analogous to the case of selenium itself¹⁶ in which the twinning of crystals with diffraction symmetry $\bar{3}m$ leads to apparent symmetry $6/mmm$. Thus the most probable space groups to which the fibrous $S_{0.56}Se_{0.44}$ belongs are $P3_1$ or $P3_2$.

The asymmetric unit of the structure contains three atoms. With one z-coordinate fixed to define the origin, there are a total of eight positional parameters and eighteen anisotropic thermal parameters. The trial values of the positional parameters were deter-

mined from a model of the structure. The structure is illustrated in Figure 4.

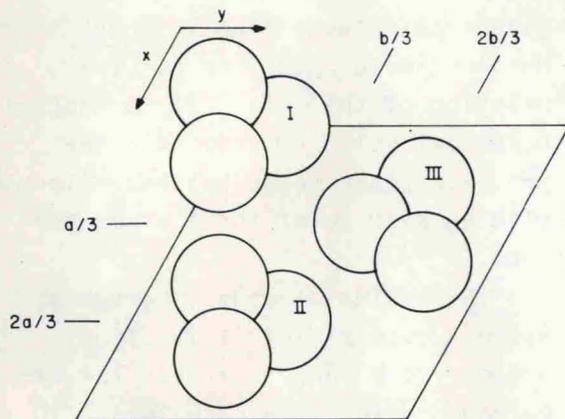


Fig. 4. Projection of $S_{0.56}Se_{0.44}$ structure along the c -axis.

Visually estimated data from $hk0$, $hk1$, $hk2$, and $hk3$ Weissenberg photographs ($CuK\alpha$ radiation) were used for the least-squares refinement of the structural parameters. The thermal parameters were kept isotropic at first and were allowed to be anisotropic in the later stages of the refinement procedure. The scattering factors (corrected for the real part of the dispersion) used were a weighted average corresponding to an atom made up of $5/9$ S and $4/9$ Se. The scattering factor multipliers for the three independent atoms were varied in the least-squares analysis to allow for non-uniformity in their compositions.

The multipliers, thermal parameters, and scale factors were not allowed to vary simultaneously.

The refinement procedure was continued until all parameter changes were negligibly small and the discrepancy factor had decreased to 0.10. At this time, the values of the multipliers indicate that the compositions of the three independent helical molecules are not equal. We now intend to determine an average scattering factor for each independent atom based on the final values of the multipliers and to carry out additional least-squares iterations using these scattering factors.

About two months after we had finished taking the first photographs involving perhaps a total exposure of less than 50 hr (mostly to $CuK\alpha$ radiation), we found that the crystal had begun to change: it appeared to be exsolving a phase isostructural with the pressure-induced fibrous sulfur. This was ascertained from an oscillation photograph about the c -axis of the $S_{0.56}Se_{0.44}$ crystal to which the fiber-axis of the sulfur II phase was exactly parallel. Two and one-half years later, an oscillation photograph still showed the presence of the hexagonal sulfur-selenium phase but a lot more of the fibrous sulfur type phase. Strangely enough, this decomposition did not take place in the original specimen