

parallel to the helix axis, the tellurium helix must have  $3n$  atoms. Therefore, the lattice constant in this direction must be close to  $7c_{Te} = 41.49 \text{ \AA}$  or  $P_s = 4.4 \text{ \AA}$ , and the formula of the phase is  $Te_7S_{10}$ .

Now we look at the van der Waals or packing diameter of the Te and S helices. In the Te case, this diameter is simply equal to the lattice constant  $= 4.457 \text{ \AA}$ . In the fibrous sulfur case, the sulfur helices are essentially hexagonally close-packed, although perhaps somewhat more efficiently (11) than those of Te, because of the simultaneous presence of both right- and left-handed helices. Examination of a scale model indicates that a very probable arrangement of helices is similar to that (2, 11) in fibrous sulfur, namely rows of right(left)-handed sulfur and left(right)-handed tellurium helices alternating along the pseudoorthorhombic  $b$ -axis (Fig. 2). If this is the case, then the pseudoorthorhombic  $b$ -axis would be equal to that of sulfur, namely  $9.25 \text{ \AA}$ . Along the  $b$ -axis, one sulfur helix accounts for  $4.05 \text{ \AA}$ ; in tellurium  $a_{Te} \sqrt{3}/2 = 3.860$ . The average of these two values is  $3.955 \text{ \AA}$  which, when multiplied by 8, predicts  $31.64 \text{ \AA}$  for the pseudoorthorhombic  $b$ -axis of  $Te_7S_{10}$ .

In our earlier experiments we had established that the new phase melts incongruently at high pressure, which, in retrospect, is a logical consequence of the absence of chemical bonding between the tellurium and sulfur atoms. Thus it appeared that it would not be possible to obtain single crystals of a size suitable for obtaining diffraction data. But the weight of the evidence nevertheless favors the plausibility of the conclusion that the structure consists of a cocrystallization of tellurium and sulfur helices in 1 : 1 ratio.

Tellurium and sulfur of 99.999+ percent purity (obtained from American Smelting and Refining Company) were finely ground. Amounts of each appropriate to  $Te_7S_{10}$  and for two high-pressure runs (to obtain sufficient material for a density measurement) were weighed out (the total weight being about  $0.41 \text{ g}$ ) and thoroughly mixed. The specimens were pressurized at  $40 \text{ kb}$  and  $400^\circ$  to  $412^\circ\text{C}$  for 4 to 5 days. The powder x-ray diffraction photographs indicated that the resulting material was single phase. The material from the two runs was ground in an agate mortar and then highly compressed in a cylindrical die with a nom-

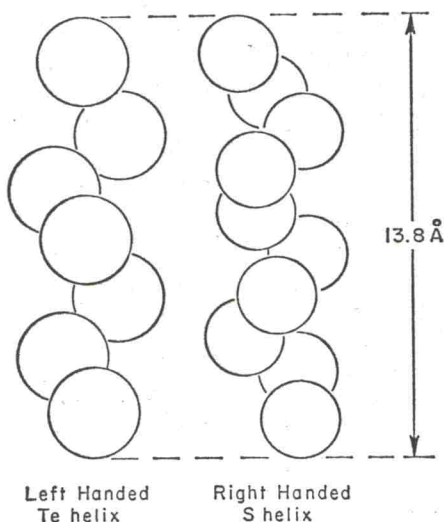


Fig. 1. The relation of the sizes of a seven-atom increment of Te helix to a ten-atom increment of S helix.

inal diameter of 0.25 inches (0.64 cm). The resulting pill had high metallic luster (as does tellurium itself) and, I believe, was close to theoretical density. The dimensions of the pellet were measured, and the pellet was weighed. The measured density was  $4.017 \text{ g/cm}^3$ .

Now, if the reasoning presented earlier is correct, the pseudoorthorhombic cell of  $Te_7S_{10}$  should have lattice constants  $a = 41.49$ ,  $b = 31.64$ ,  $c = 9.25 \text{ \AA}$ ; in indexing of the powder photograph (Table 1), I reduced  $c$  to  $9.24 \text{ \AA}$ . With  $8 \times 30 = 240$  S atoms, and  $8 \times 21 = 168$  Te atoms in this cell, the calculated x-ray density is  $3.99 \text{ g/cm}^3$ , which is within less than 1 percent of the measured value.

It should be emphasized that it is really impossible for the structure of the  $Te_7S_{10}$  phase to have orthorhombic symmetry (2). The monoclinic cell de-

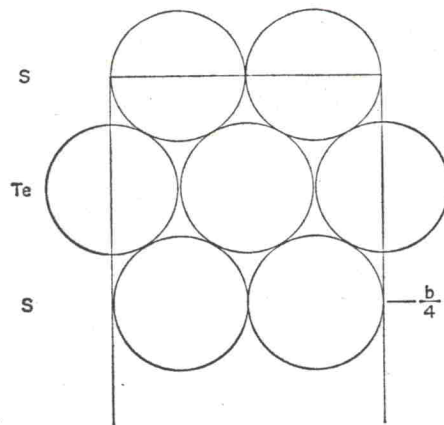


Fig. 2. Idealized packing of the S and Te helices. The circles, drawn to scale, represent projections of the van der Waals "cylinders" circumscribing the helices.

rived from the end-centered pseudoorthorhombic cell has lattice constants:  $a = 41.49$ ,  $b = 9.24$ ,  $c = 26.09 \text{ \AA}$ ,  $\beta = 142.7^\circ$ . To have monoclinic symmetry, the twofold symmetry of some of the sulfur helices must be used. For efficient packing of the tellurium and sulfur helices, however, this could turn out not to be possible, and in view of our results on the fibrous sulfur (2), improbable. In this case, the most probable space group for the phase would be  $P1$ .

One further point should be made regarding the fibrous sulfur itself. In my earlier report (1), I had indicated that the pressure-induced modifications were obtained only when the sulfur was first melted and then held at temperature and pressure for some time. For the temperatures given in that report, this is correct. However, I could not escape the logical conclusion that the formation of the new  $Te_7S_{10}$  phase below the melting point of either sulfur or tellurium implied that melting is not required for the formation of helical sulfur molecules. I therefore ran an experiment in which sulfur was pressurized to  $40 \text{ kb}$  and held at  $400^\circ\text{C}$  for 4 days. The resultant product was indeed the fibrous modification. Sclar et al. (11) have also reported obtaining this phase without having first melted the sulfur (see also 12).

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