

PRESSURE INDUCED PHASES IN THE CHALCOGENS

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ABSTRACT

Several quenchable pressure-induced phases involving the chalcogens have been found. Structural investigations indicate that all contain helical molecules. In at least three of these, Sulfur II, $S_{0.56}Se_{0.44}$ and Te_7S_{10} , the helices are arranged in a two-dimensional nearly hexagonal array, with some relative shifts along the helix axis and relative rotations to insure optimum packing. Thus far, the most detailed structural work has been done on fibrous sulfur (II) and on $S_{0.56}Se_{0.44}$.

INTRODUCTION

In the past three or four years, we have given some attention to the effect of high pressure on the chalcogens and intimate mixtures or solid solutions thereof.¹⁻⁴ As a result, several pressure-induced phases which can be retained for long periods of time at atmospheric pressure have been obtained. Crystallographic investigations support the conclusion that the

phases we have found all have helical molecules involving only two-coordination as would be expected for sulfur and selenium, but perhaps not for tellurium. In the case of tellurium itself two pressure-induced phases, not quenchable, have been found by others (see Ref. 5 for appropriate references). One of these, which exists at pressures greater than 70 kb, has the β -polonium structure;⁵ the structure of the other is still unknown.⁵

SULFUR

There are at least three metastably retainable pressure-induced phases of sulfur obtainable¹ at pressures below about 30 kb. Our technique for obtaining these was first to melt the sulfur under pressure, then to anneal it for some time at a given temperature below the melting point, then to quench it. At first it was believed that melting was required initially to obtain complete conversion in reasonable time. However, in the case of the

fibrous form at least, Sclar et al.⁶ had found that the transformation occurred without initial melting. To understand the formation of Te_7S_{10} (see below) this seemed to be required. Thus we carried out an experiment³ on sulfur which confirmed the Sclar et al.⁶ result.

In the structural work,⁴ we have given most attention to the fibrous phase, mainly because it was the most tractable. Our experiments gave us the best crystals of this phase (II) although they were not truly single crystals. We obtained crystals of the lamellar phase (I), but the twinning is quite complicated. We could not seem to obtain crystals of the phase we have labeled III.

The paper⁴ on the structural investigation of the fibrous phase is now in press. The pressure-induced phase II appears to be identical with ψ -sulfur first unequivocally identified by Prins and coworkers,⁷ although not first obtained by them.⁸ Prins and coworkers^{7,9,10} obtained the ψ -sulfur by stretching plastic sulfur, washing it with CS_2 , and annealing it at 80°C for 40 hr. The identification was mainly by a fiber x-ray diffraction pattern. As shown by us^{1,4,11} they did not find the correct unit cell although they did find the correct fiber axis repeat

distance.

Most important, however, Prins et al.⁷ were the first to propose the correct structure of the sulfur molecule, and while the x-ray data from the "single" crystals of the pressure-induced fibrous sulfur allowed prediction that the structure must contain both right- and left-handed helical molecules,¹ Prins and Tuinstra¹⁰ made this proposal earlier from geometric considerations. However, a subsequent paper¹² by Tuinstra on ψ -sulfur appears to be at least partially incomprehensible. Further, some comments made by Tuinstra¹³ regarding the unit cell determination appear to have no merit.

The crystals of the pressure-induced fibrous phase have apparent diffraction symmetry mmm. They also clearly show in the diffraction photographs a pseudo-hexagonal rotation twinning¹ and in the course of the analysis, correction of intensities for overlap of some of the reflections was made. However, we soon found that to account for the intensities and the diffraction symmetry there must be a further much more subtle twinning present. In fact, the crystals most probably belong to space group $P2_1$, the mmm symmetry resulting from a fine-grained mirror twinning.

The pseudoorthorhombic-cell

has lattice constants $a = 13.8 \text{ \AA}$ (fiber axis), $b = 32.4$, $c = 9.25 \text{ \AA}$. The true primitive monoclinic cell has axes $a = 17.6$, $b = 9.25$, $c = 13.8 \text{ \AA}$, $\beta = 113^\circ$. The relation between the two cells is shown in Fig. 1. The mmm symmetry is caused by pseudoorthorhombic (100) or (010) twinning of enantiomorphs.

The nature of the structure causes the absence of large classes of reflections, which are not space group absences. On the pseudoorthorhombic basis, reflections with $h = 0, 3, 6, 8, 9$, l odd and $h = 1, 2, 4, 7, 10$, l even were absent. Also no reflection $h00$ was observed to $h = 20$. In the $\text{CuK}\alpha$ sphere of reflection a total of 429 reflections was observed.

We built a model based on our lattice constants and having three-dimensional order but otherwise having an arrangement similar to that proposed by Prins and Tuinstra.¹⁰ The model incorporated the prior proposal of Prins et al.⁷ that the sulfur helix has a 13.8 \AA period containing ten atoms in three turns of the helix. The model showed that, at least ideally, the space group of the fibrous modification is P2. The arrangement takes advantage of the twofold axes of the $^{10}S_3$ helices; twofold axes, intersecting the helix at right angles, pass through the center of

each atom and through points halfway between each pair of atoms (see Fig. 2).

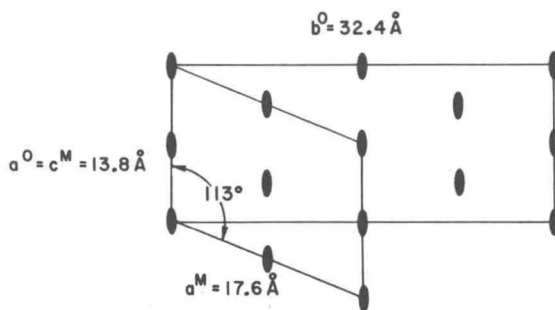


Fig. 1. Relationship between primitive monoclinic (M) and C-face centered orthorhombic (O) unit cells.

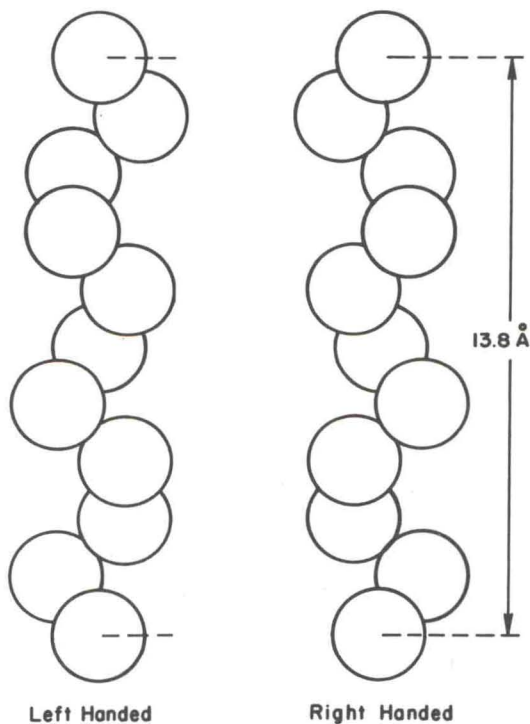


Fig. 2. Idealized sulfur helices.

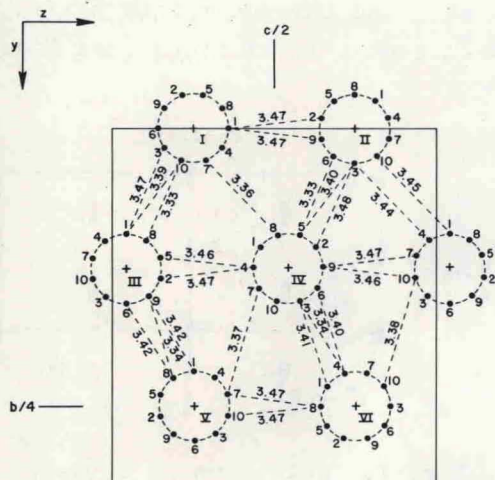


Fig. 3. Projection of the sulfur (II) structure along the fiber axis.

The arrangement is illustrated in Fig. 3. A description based on the pseudo-orthorhombic C-face centered unit cell rather than the primitive cell was used in the structure analysis to facilitate treatment of the twinning. In this description the coordination of the equivalent positions of space group P2 are x, y, z ; \bar{x}, \bar{y}, z ; $\frac{1}{2} + x, \frac{1}{2} + y, z$; and $\frac{1}{2} - x, \frac{1}{2} - y, z$. These may be used to derive the remainder of the unit cell not shown in Fig. 3. In the figure, the numbering of the atoms in each helix begins with the atom nearest to $x = 0$. The rows of helices parallel to c have the same hand but in successive rows in the b direction,

the hand alternates. Helices I, II, V, and VI are shown as right-handed and helices III and IV as left-handed; these are reversed in the enantiomorph. Eight of the 160 sulfur atoms per unit cell are on twofold axes; these are atoms 1 and 6 of helix I, atoms 3 and 8 of helix VI, and their four equivalents. The remainder of the atoms are in general positions. There are 42 atoms in the asymmetric unit. The structure has 117 independently variable positional parameters and 244 independently variable anisotropic thermal parameters.

Needless to say the total number of observable data, 429, was inadequate for refinement of the total number of parameters, 361 (excluding scale factors). The number of positional parameters was decreased to twelve by assuming the sulfur molecules to be ideal $^{10}\text{S}_3$ helices. An overall isotropic temperature factor and a scale factor were adjusted separately. Attempts at refinement of the twelve positional parameters indicated strong correlations between certain pairs and produced large oscillatory parameter changes.¹⁴ When the correlated parameters were deliberately specialized or coupled, reducing the number of variables to

five, convergence was attained.

The agreement of calculated with observed structure amplitudes shows that the results are at least approximately correct. For the 429 observable data, the discrepancy factor is 0.16. Of the 436 data (not included among those systematically absent) below threshold, 388 have $|F_{\text{calc}}|$ below the minimum observable $|F_{\text{obs}}|$ and 48 have $|F_{\text{calc}}|$ greater than threshold values, in most cases, only slightly greater. For all the reflections systematically absent, the $|F_{\text{calc}}|$ was less than the minimum observable value. This overall agreement is satisfactory considering the nature of the crystals and the necessary idealization of the structure.

The structure of the helical molecule was given only one variable, namely, the radius, r , in the least-squares analysis. Because the final value of r , 0.95 Å, is very near that given by Prins et al.⁷ the structure of the molecule remains very much like the one they described: The S-S distance is 2.07 Å and the S-S-S bond angle, 106°; the shortest non-bonded S-S distance is 3.30 Å and the dihedral angle $S_1S_2S_3 - S_2S_3S_4$ is 95°.

None of the large number of intermolecular distances (Fig. 3) is significantly shorter than 3.37 Å, the shortest intermolecular distance

previously reported for sulfur.

We have indicated earlier that the pressure-induced fibrous modification of sulfur is identical with ψ -sulfur. The rotation photograph about the fiber axis of a crystal of the pressure-induced phase exactly matches that of a fiber pattern of ψ -sulfur. The literature¹² contains erroneous conclusions regarding the indexing of this pattern. For completeness, we give here (Table 1) our indexing based on the pseudo-orthorhombic cell and confirm that the data obtained by Tuinstra from the fiber pattern of ψ -sulfur agree with those from the pressure-induced phase. There is greater resolution in our data, however. (We hope to have a somewhat more detailed discussion of this indexing published elsewhere).

The crystals of the fibrous phase of sulfur have remained intact (at atmospheric pressure and room temperature), that is, with no apparent transformation to any other phase, for a period of approximately 3½ years.

With respect to phase (I), we have proposed that it is probable that the sulfur helical molecules lie in planes perpendicular to a 32.4 Å repeat distance as in the fibrous phase, but because it is lamellar, the helices are skew to each other in alternating planes. Phase I has

Table 1. Indexing of Rotation Photograph of Ψ -Sulfur

Tuinstra				Present Work				Tuinstra				Present Work				Tuinstra				Present Work									
Q _o	Q _o	Q _c	h k l	Q _o	Q _o	Q _c	h k l	Q _o	Q _o	Q _c	h k l	Q _o	Q _o	Q _c	h k l	Q _o	Q _o	Q _c	h k l	Q _o	Q _o	Q _c	h k l	Q _o	Q _o	Q _c	h k l		
473	478	467	002	*	2625	2634	2,12,3					3792	3774	3759	4,14,3														
613	613	610	080	*	3253	3284	245						3826	3800	425														
		620	042	*	3713	3701	2,16,3					4093	4036	4043	4,18,1														
1842	1847	1839	0,12,2	*	4092	4137	2,20,1					4751	4719	4715	4,10,5														
2050	2046	2022	044	*	4451	4501	2,12,5					*	5639	5629	4,14,5														
2431	2422	2439	0,16,0	*	5582	5570	2,16,5					*	6472	6503	4,22,3														
2470	2475	2480	084	*	5839	5814	2,24,1					*	6957	6910	467														
2868	2894	2906	0,16,2	*	6099	6089	247																						
3244	3234	3242	0,12,4	*	6610	6547	287					2250	2230	2233	660														
4265	4271	4208	006									2379	2372	2396	622														
		4278	0,20,2	946	950	939	370					2707	2706	2701	662														
4316	4345	4309	0,16,4	*	1032	1026	332					2800	2823	2843	6,10,0														
4845	4843	4817	086	1165	1160	1178	352				3284	3300	3311	6,10,2															
5449	5455	5487	0,24,0	1222	1224	1244	390				3797	3807	3798	624															
5618	5619	5579	0,12,6	1414	1414	1407	372				4172	4089	4103	664															
		5680	0,20,4	1691	1706	1712	392				*	4762	4712	6,10,4															
*	6631	6646	0,16,6	2104	2107	2093	3,11,2				*	4923	4977	6,18,0															
					2377	2352	314				*	5484	5444	6,18,2															
962	967	941	191		2431	2428	334				*	5640	5628	6,14,4															
1146	1133	1113	113	2500	2532	2550	3,13,2				*	6171	6136	626															
1300	1318	1322	1,11,1		2578	2581	354				*	6521	6501	6,22,0															
1361	1380	1342	153			2616	3,15,0				*	6952	6968	6,22,2															
1933	1934	1876	193	3110	3099	3083	3,15,2				*	7070	7050	6,10,6															
2250	2251	2257	1,11,3			3114	394																						
2978	2948	2922	1,17,1	*	3171	3226	3,17,0				2732	**	2699	711															
3113	3086	3060	135	3517	3489	3495	3,11,4				2808	**	2776	731															
3255	3233	3212	155	*	5547	5512	3,23,0				2950	**	2928	751															
		3248	1,15,3	*	6295	6290	3,13,6				3470	**	3461	791															
3470	3454	3441	175	*		7885	3,27,2				3712	**	3710	733															
3560	3548	3608	1,19,1	*	7916	7962	318				3867	**	3843	7,11,1															
3790	3750	3746	195	*	8263	8296	3,25,4					**	3863	753															
3860	3875	3857	1,17,3	*	8856	8881	3,21,6				4136	**	4092	773															
5130	5135	5118	1,15,5	*	9270	9287	3,27,4				4337	**	4397	793															
		5789	117																										
5900	5858	5865	137	1318	1316	1300	461				5414	**	5406	10,2,1															
		6123	1,25,1	1942	1936	1910	4,10,1				5550	**	5520	10,4,1															
6200	6096	6144	1,23,3			1930	423				6017	**	5978	10,8,1															
		6246	177	2250	2253	2235	463																						
*	7005	6932	1,11,7	2866	2856	2824	4,14,1																						
		7058	1,25,3			2844	4,10,3																						

* Not reported by Tuinstra.

** Not measured in present work.

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.

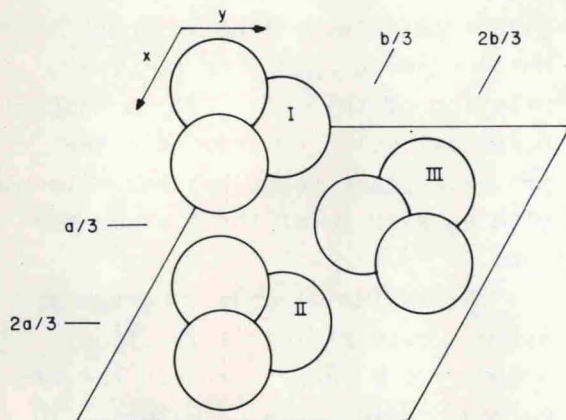


Fig. 4. Projection of $S_{0.56}Se_{0.44}$ structure along the c -axis.

Visually estimated data from $hk0$, hkl , $hk2$, 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

which had not been irradiated at all. The powder photograph recently taken of the pressure-induced sulfur-selenium phase made 2-1/2 years ago is the same as that taken 2-1/2 years ago, that is, none of the fibrous sulfur (II) type phase is present. This implies that the irradiation began the decomposition of the crystal used to obtain the data for the structure determination.

SULFUR-TELLURIUM

Prior to the work³ on sulfur-tellurium that was done in our laboratory, no phase simultaneously involving these two elements was known. Inasmuch as the information on the new phase has already been published, we shall only summarize the results here.

The new phase is found only by reaction in the solid state; melting causes segregation of sulfur and tellurium. The phase has the formula Te_7S_{10} and was prepared by pressurizing an intimate mixture of appropriate proportions of Te and S at 40 kb and 400-412°C for 4 to 5 days. Crystal chemical and geometric considerations led to the deduction of the correct formula of the phase and to a proposed atomic arrangement in it.

At first, high pressure experiments with various proportions of Te and S led to the conclusion

that the chemical formula of the phase was very close to Te_3S_4 which could not be a valency compound. The x-ray powder diffraction lines occurring in the powder patterns of all specimens established that there was no solid solution range in the phase. The other phases which appeared were hexagonal Te on the Te rich side and fibrous sulfur (II) on the sulfur rich side. It turns out that a seven atom increment of the Te helix is, within experimental error, the same length as a 10 atom increment of the sulfur helix (Fig. 5) and the van der Waals "cylinders" (Fig. 6) of the two have very nearly the same radius. Thus the lattice constants of a pseudoorthorhombic cell could be deduced for this phase. Because the Te helix has three atoms per turn, the repeat distance along the helix axis must be three times that of the seven atom increment of Te helix. The pseudoorthorhombic cell has lattice constants $a = 41.49$, $b = 31.64$, $c = 9.24$ Å. (The monoclinic cell has $a = 41.49$, $b = 9.24$, $c = 26.09$ Å, $\beta = 142.7^\circ$) An idealized packing scheme of the proposed sulfur and tellurium helices is shown in Fig. 6.

The pseudoorthorhombic cell contains 240 S and 168 Te atoms leading to an x-ray density of 3.99 g/cm^3 as compared with a

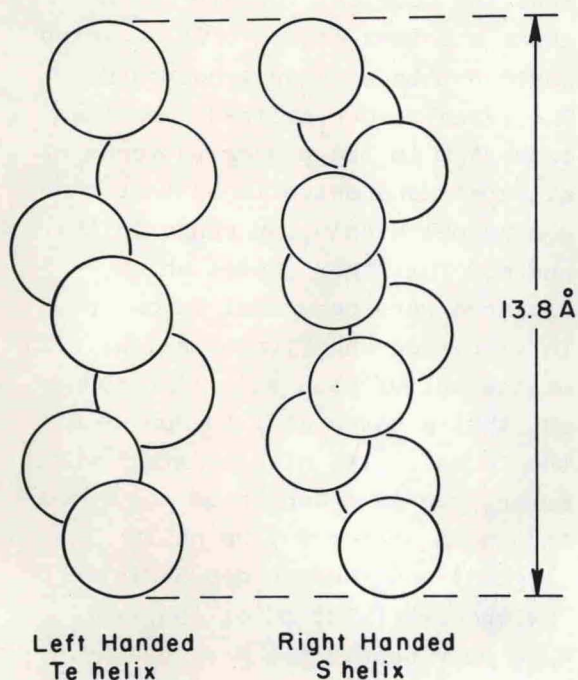


Fig. 5. The relation of the sizes of a seven-atom increment of Te helix to a ten-atom increment of S helix.

measured density of 4.02 g/cm^3 . Further the lattice constants given above allowed a completely satisfactory indexing of the powder pattern.

TERNARY PHASES

Preliminary experiments have revealed the existence of at least three pressure-induced ternary phases.

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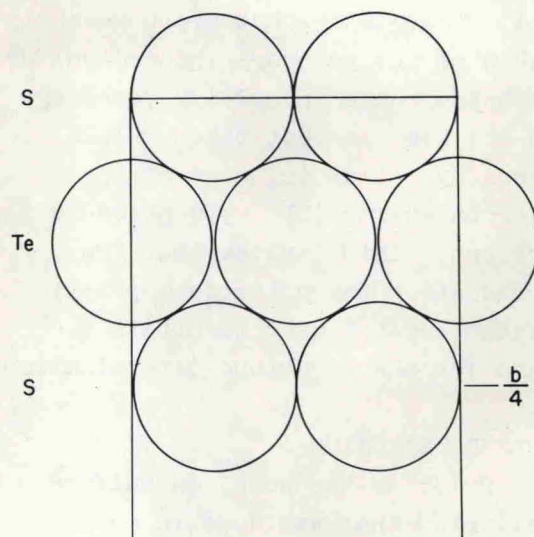


Fig. 6. Idealized packing of S and Te helices. The circles, drawn to scale, represent projections of the van der Waals "cylinders" circumscribing the helices.

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