

PRESSURE INDUCED PHASES IN THE CHALCOGENS

S. Geller and M. D. Lind

Science Center, North American Rockwell Corporation
Thousand Oaks, California

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 pseudohexagonal 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, the mmm symmetry resulting from a fine-grained mirror twinning.

The pseudoorthorhombic-cell