Using arguments analogous to those presented for the assignments of the CF_4 spectrum and the participation of d orbitals in the bonding for silicon leads us to assign the first two bands in the spectrum of SiF_4 to the two triply degenerate orbitals t_1 and $4t_2$, respectively. The participation of d orbitals of silicon invalidate the use of the empirical "center of energy" concept used in the CF_4 assignments because the e level is no longer totally fluorine localized. The third band (IP = 18.09 eV) is assigned to the removal of electrons from the $4a_1$ level for three reasons. First, it is unlikely that the two sets of t_2 orbitals are only 0.5 eV apart[20] and, second, although the relative intensities are somewhat uncertain, the intensity of this band suggests that it is not triply degenerate. Third, the outermost a_1 level in CF_4 and SiF_4 is bonding with carbon 2s and silicon 3s, respectively. The energy of the carbon 2s lies below that of the silicon 3s which should tend to raise the a_1 bonding orbital in SiF_4 relative to CF_4. Since the e level has been assigned to the fourth observed band of SiF_4 on the basis of the vibrational structure, the $3t_2$ level is apparently below 21.22 eV.

Experimental Section

The apparatus and procedures used to obtain the photoelectron spectra reported here have been described previously[9] in detail. The spectrometer, located at Oak Ridge National Laboratory, is a double-focusing spherical-plate electrostatic spectrometer. A preacceleration of 10 V was given the electrons before analysis. The kinetic energies plotted in Figures 1 and 2 are not measured kinetic energies but have been related to the binding energies of standard gases Ar, Kr, and Xe, as measured in separate experiments using mixtures of the sample gas and these standard gases. All compounds were used as received from Olin-Mathieson with stated purity of 99.7% for CF_4 and 99.6% for SiF_4.

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(20) We thank one of the reviewers for calling this point to our attention.

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The Ring → Chain High-Pressure Polymorphic Transformation in Sulfur and the Accompanying Change from Insulating to Modest Semiconducting Behavior

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A high-pressure, high-temperature crystalline form of sulfur, having major X-ray reflections at *d* spacings 4.04, 3.23, and 2.90 Å and designated sulfur XII, has been synthesized in a hexahedral apparatus and quenched to ambient conditions. Studies of the thermally quenched product by X-ray diffraction and by Raman and infrared spectroscopy show that this phase is not based on the octameric puckered-ring structure of orthorhombic sulfur I stable at ambient conditions but on a chain-type structure similar to selenium and tellurium. X-Ray diffraction studies taken at ambient conditions many months after synthesis show that helical sulfur XII does not revert to octameric sulfur I. Photoelectric and epr studies of the thermally quenched product and *in situ* electrical measurements indicate that sulfur XII has the properties characteristic of a modest semiconductor.

Introduction

The stable equilibrium form of sulfur at ambient conditions is based on the stacking of eight-membered puckered rings and is an insulator with a resistivity of about 10^{17} ohm-cm. However, in a detailed study of the polymorphism of sulfur up to 100 kbars and 500° Vezzoli, Dachille, and Roy[1] found evidence of 11 other crystalline phases of sulfur. These phases were not characterized electrically, and of them, only the highest pressure, highest temperature phase, designated sulfur XII, could be retained (for more than 3 years) upon thermal quenching. We have synthesized a substantial volume of this same phase in a hexahedral apparatus,[2] and the purpose of this paper is to describe the structure and properties of sulfur XII and show its resemblance to the well-known semiconductors selenium and tellurium, which are also members of group VIa.

The pressure–temperature (p–T) field in which sulfur XII was synthesized is given by Vezzoli.[3] Under similar p–T conditions, other investigators also synthesized quenchable phases of sulfur. These are denoted as fibrous sulfur or phase II by Geller,[4] the 4.04-Å phase by Sclar, Carrison, Gager, and Stewart,[5] and fibrous sulfur by Ward and Deaton.[6] A phase which upon thermal quenching gave a single X-ray diffractometer peak at *d* spacing 4.04 Å was reported earlier by Baak[7] but was attributed to preferential orientation from the melt.

Geller[4] and more recently Lind and Geller[8] showed further that fibrous sulfur has orthorhombic diffraction symmetry but actually belongs to space group *P*2 and is based on nearly hexagonally closest packed right- and left-handed helices of period ten atoms with some dis-

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(1) G. C. Vezzoli, F. Dachille, and R. Roy, *Science*, **166**, 218 (1969).

(2) G. A. Samara, A. Henius, and A. A. Giardini, *J. Basic Eng.*, **86**, 729 (1964).

(3) G. C. Vezzoli, Ph.D. Dissertation, The Pennsylvania State University, University Park, Pa., 1969; *Diss. Abstr.*, **30**, No. 7 (1970).

(4) S. Geller, *Science*, **152**, 644 (1966).

(5) C. Sclar, L. Carrison, W. Gager, and O. Stewart, *J. Phys. Chem. Solids*, **27**, 1339 (1966).

(6) K. B. Ward and B. C. Deaton, *Phys. Rev.*, **163**, 947 (1967).

(7) T. Baak, *Science*, **148**, 1220 (1965).

(8) M. D. Lind and S. Geller, *J. Chem. Phys.*, **51**, 348 (1969).

order present about the helix axis and eight helical segments per monoclinic unit cell. This helical structure is very similar to the spiraling zigzag chain structure of sister elements selenium and tellurium at ambient conditions. Further similarity between fibrous sulfur and tellurium is also afforded by Geller,[9] who was able to cocrystallize at high pressure and high temperature spiraling helices of these two materials as Te_7S_{10}. Since the X-ray diffraction powder patterns for Geller's fibrous sulfur,[4] for phase XII,[3] and for the 4.04-Å phase of Sclar, *et al.*,[5] were essentially the same (with the exception of a few missing very weak reflections), within the margin of experimental error we felt that these phases were identical, and thus sulfur XII is based on a helical-chain structure.

Further indication that sulfur XII has a chain-type structure can be derived from the high-pressure study of liquid sulfur by Vezzoli, Dachille, and Roy[10] in which it was consistently observed that the product quenched thermally (designated sulfur liquid E) from the liquid phase field in equilibrium with sulfur XII was a highly stretchable "rubbery" viscoelastic polymer giving a characteristic X-ray diffraction reflection at d spacing 4.52 Å. This viscoelastic metastable product is insoluble in CS_2 and physically resembles CS_2-insoluble sulfur, a polymeric material formed by the slow cooling of the sulfur melt. Thus it was suggested that liquid E has a "fiber structure" and is probably composed of long sulfur chains. This is supported by the prediction[11] and observation[10] by differential thermal analysis methods that the p–T polymerization curve for sulfur intersects the melting curve at about 1 kbar so that above this pressure sulfur melts directly to polymeric chains. Then on the basis of structural continuity across the liquidus, for which some evidence exists in selenium and tellurium,[12] it was inferred that sulfur XII has a chain-type structure similar to the structures of these closely related elements at ambient conditions.

Experimental Section

A hexahedral high-pressure, high-temperature apparatus as described by Samara, Henius, and Giardini[2] was utilized to synthesize sulfur XII from a starting material of high purity (99.9999%) octameric orthorhombic sulfur (designated sulfur I) purchased from The American Smelting and Refining Co. and stored in a vacuum desiccator. The sample chamber consisted of a boron nitride furnace cylinder which was coaxially enclosed in a stainless steel heater tube that fitted snugly in the center of a pyrophyllite cubic pressure block that measured 5.7 cm on an edge. The finely powdered sample was packed in the center of the boron nitride furnace and occupied a cylindrical section of r = 1.43 cm and h = 0.95 cm. Pyrophyllite plugs occupied the excess volume in the furnace and were isolated from the sample by tantalum foils. Pressures were not hydrostatic, but previous experience showed that the chamber was suitable for the synthesis of large amounts of sample (about 1.5 cm^3) with small pressure gradients. Four leads extending from the sample through the pyrophyllite cube to the anvils were used for temperature and resistance measurements and were insulated from the heater tube by pyrophyllite sleeves. Brass cylinders with pyrophyllite inserts fit snugly against the heater tube and made contact with the anvils *via* brass disks. Good electrical contact between leads and anvils was ensured by the use of copper or aluminum foils on the faces of the pyrophyllite cube. Two lead measurements of resistance were made with tantalum electrodes in the first experiment and copper electrodes in the second, and the resistance was continuously monitored with the use of a dc vacuum tube voltmeter used in conjunction with a Brush Mark 240 recorder. Previous experience has shown that relative resistance changes associated with phase changes could be measured in this manner and were adequate to calculate rough resistivities (orders of magnitude).

In our apparatus, temperatures were measured with a chromel–alumel thermocouple imbedded in the center of the sample and believed to be accurate to ±4°. Later experiments[13] utilizing two additional gasket leads enabled a temperature measurement at a peripheral thermocouple and showed that at the temperatures of the experiments on sulfur approximately a 12° thermal gradient existed across the center plane perpendicular to the axis of the cylindrical sample.

The normal room-temperature bismuth calibration for a similar sample chamber which had been used by Samara, *et al.*,[2] was slightly modified by utilizing the previously determined melting curve of sulfur.[14] This type of calibration precluded error introduced by the difference between the elastic behavior of the sample and that of the calibrant which is apt to have a measurable effect in a system with a large pressure chamber, and ensured that pressure was calibrated at the approximate temperature at which sulfur XII was to be synthesized. The pressure calibration was checked by measuring the melting temperature of tellurium at several values of elevated pressure and found to be in good agreement with the tellurium melting curve reported by Klement, Cohen, and Kennedy.[15] The resulting pressure calibration, based on a three-point calibration for both sulfur and tellurium, showed that in the temperature range of this experiment, pressures should be accurate to ±5–10%. It is perhaps worthy to mention that this calibration agreed to within ±3% of the room-temperature calibration of true pressure *vs.* load in a high-pressure chamber having similar dimensions but containing a liquid as the compressing media.[16]

Pressure was raised at first to about 3 kbars where it was held for 45 min to allow stresses to reach equilibrium, after which the pressure was raised in small increments every few seconds at an average rate of about 200 bars/min until achieving a pressure of about 35 kbars. The temperature was then slowly increased by raising heater voltage in small increments every 5 min (corresponding to an average heating rate of about 7–12°/min) until a temperature of 415° was reached. The conditions of synthesis of 35 kbars and 415° were chosen in an effort to ensure that the charge was safely inside the stable phase field of sulfur XII[1,3–6] and at low enough pressure and high enough temperature to crystallize the phase rapidly.[3,17]

The sample was held at about 35 kbars and 415° for 3 hr after which the temperature was quickly lowered to 20°. The run was then held at pressure overnight, after which the temperature was again raised (at constant pressure) to around 415° and held at approximately this value for 6 hr more before quenching temperature and then slowly releasing pressure.[18] The purpose of the second heat treatment was to test the reproducibility of the electrical resistance *vs.* temperature curve and to allow more time for the expected phase transformation to proceed to com-

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[9] S. Geller, *Science*, **161**, 290 (1968).

[10] G. C. Vezzoli, F. Dachille, and R. Roy, *J. Polym. Sci., Part A-1*, **7**, 1557 (1969).

[11] A. Eisenberg, *J. Chem. Phys.*, **39**, 1852 (1963).

[12] A. S. Epstein, H. Fritzsche, and K. Lark-Horovitz, *Phys. Rev.*, **107**, 412 (1957).

[13] G. C. Vezzoli, to be submitted for publication.

[14] G. Vezzoli, F. Dachille, and R. Roy, *Inorg. Chem.*, **8**, 2658 (1969).

[15] W. Klement, Jr., L. H. Cohen, and G. C. Kennedy, *J. Phys. Chem. Solids*, **27**, 171 (1966).

[16] J. Barnett and C. Bosco, *Rev. Sci. Instrum.*, **38**, 957 (1967).

[17] G. C. Vezzoli and F. Dachille, *Inorg. Chem.*, **9**, 1973 (1970).

[18] In the present experiment quenching was accomplished by very rapid cooling (300°/min) followed by a moderately slow release of pressure (50 bars/min). In all cases, temperature was always quenched first to avoid melting the high-pressure phase; thus we have the phrase "thermally quenched product."

pletion. During the holding periods, the pressure and temperature fluctuations were ±0.7 kbar and ±5°.

A second experiment was then conducted in which sulfur was melted at 35 kbars at 555°, held for 1 hr at pressure and temperature, and then thermally quenched in order to compare the product with sulfur liquid E which had been observed in the previous high-pressure study of liquid sulfur.[10]

Results and Discussion

Structural Characterization of Sulfur XII.—The diffractometer and Debye–Scherrer X-ray patterns, taken at room conditions of the thermally quenched product, gave no evidence of impurities nor of reaction with any components of the pressure chamber (pyrophyllite, boron nitride, tantalum, etc.). The *d* spacings and relative intensities from Debye–Scherrer photographs of sample specimens which were taken from the center of the sample chamber are presented in Table I and indicate that sulfur XII is essentially identical with fibrous sulfur[4] and with the 4.04-Å phase.[5]

TABLE I
X-RAY DIFFRACTION DATA FOR HELICAL SULFUR XII
(COPPER Kα RADIATION)[a]

d, Å	Rel intens	*d*, Å	Rel intens	*d*, Å	Rel intens	*d*, Å	Rel intens
4.54	w	2.66	w	2.02	w	1.63	w
4.04	vs	2.40	vw	1.99	w	1.60	w
3.23	m	2.27	m	1.88	vw	1.56	w
2.90	m	2.18	vw	1.78	vw	1.54	vw
2.82	w–m	2.10	vw	1.69	w	1.35	w
						1.34	w

[a] Abbreviations: s, strong; m, medium; w, weak; v, very.

X-Ray diffractometer studies of sulfur XII showed only a single very intense peak corresponding to the *d* spacing 4.04 Å and very weak peaks corresponding to *d* spacings 3.23, 2.93, and 2.84 Å. The seems to explain why Baak,[7] using the diffractometer,[19] reported one "very strong peak at about 4.04 Å" in products thermally quenched from p–T conditions now known to be located within phase field XII just above the kinetic barrier.[3,17] Thus, Baak was actually the first to report the synthesis of the high-pressure phase which we designate sulfur XII, and the present study represents the first reported synthesis of this phase in a hexahedral apparatus.

The transformation of sulfur I to sulfur XII did not proceed to completion in regions toward the periphery of our cylindrical sample chamber because of pressure and temperature gradients. X-Ray diffractometer examination of the samples, after exposure to air at ambient conditions for 10 months after synthesis, showed that sulfur XII did not revert to sulfur I, even for those specimens that contained sulfur I, since the intensity ratio of the principal reflection of sulfur XII to that of sulfur I remained unchanged.

The residual sulfur I (octameric puckered rings) could be separated from the high-pressure sulfur XII by treating the quenched product with CS_2. Figure 1 shows diffractometer X-ray patterns of the same quenched product before and after a single treatment with CS_2. This product had of course been taken from the periphery of the sample chamber. The CS_2 treatment dissolved all the residual sulfur I that had not undergone transformation, while leaving the insoluble sulfur XII intact. Debye–Scherrer X-ray photographs of the remaining sulfur XII after the CS_2 treatment were identical with those of products that were taken

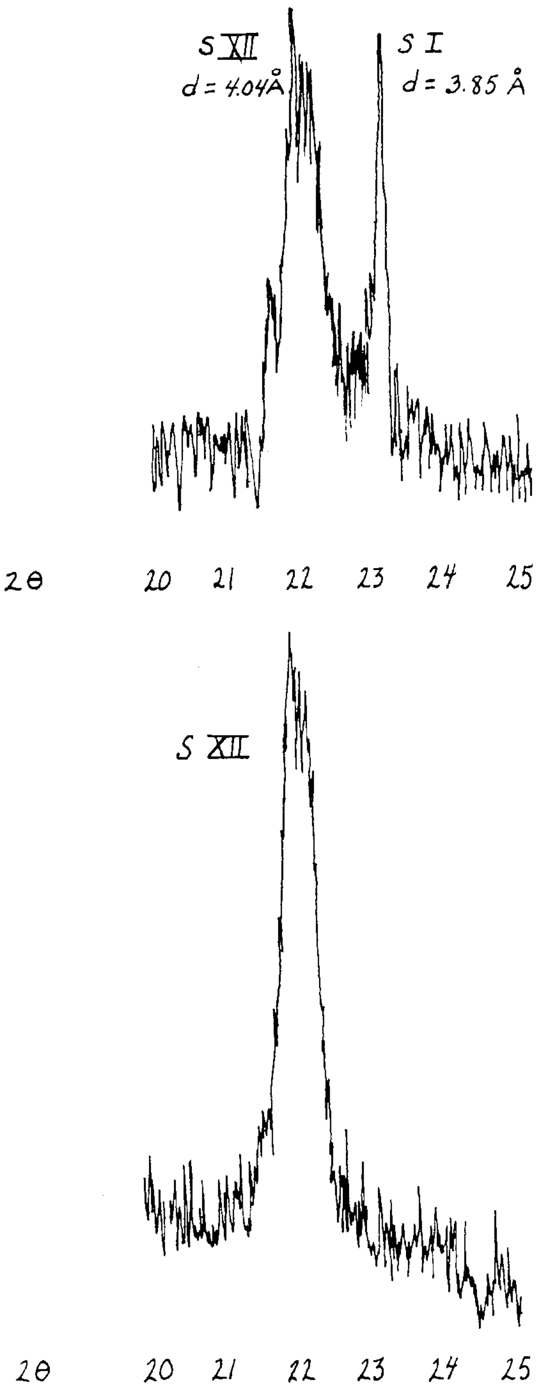

Figure 1.—Above, Norelco X-ray diffractometer pattern of thermally quenched specimen taken from the periphery of the sample chamber and containing both phases XII and I due to incomplete transformation in regions of pressure and thermal gradients; below, the X-ray pattern of the identical sample specimen after a single 5-min treatment with CS_2. All X-ray studies were taken at ambient conditions utilizing Cu Kα radiation.

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[19] T. Baak, private communication

from the center of the sample chamber where the polymorphic reaction had proceeded to completion.

The long shelf life of sulfur XII is consistent with the observations of Vezzoli,[3] Geller,[4] and Ward and Deaton[6] but does not agree with the report of Sclar, *et al.*,[5] that the 4.04-Å phase slowly inverts in air at room conditions to ordinary orthorhombic sulfur I. The apparent irreversibility of the reaction producing sulfur XII is also consistent with a chain-type structure. Von Hippel[20] has pointed out that in selenium and tellurium, the chain molecules are interlinked by so many secondary bonds that they cannot revert to ring molecules. Since the helical chain structure of sulfur XII is close packed due to the very high pressure associated with its formation, the individual helices may be attracted to each other with a large degree of van der Waals bonding which perhaps stabilizes the molecule and prevents any reversion to the ring configuration.

In our study, the product that was quenched from p–T conditions of 35 kbars at 555° had the same viscoelastic properties and X-ray diffraction pattern as sulfur liquid E which was found in the previous liquid study[10] and was metastable for longer than 1 day. This gives further support that if some structural continuity exists across the liquidus, sulfur XII should have a quenchable chain-type structure. The metastability of the polymeric viscoelastic quenched liquid indicates the presence of van der Waals bonding that might be expected to also be present in the helical solid with which the liquid is in equilibrium. Then as suggested above, it may be this van der Waals bonding that preserves the structure of sulfur XII at ambient conditions, even though this phase does not have the lowest Gibbs free energy at these conditions and thus strictly speaking is not thermodynamically stable at 1 atm and room temperature.

Additional evidence that sulfur XII is based on a structure different from that of ordinary octameric sulfur I is derived from Raman spectra of the polycrystalline thermally quenched product. A Raman spectral analysis using a Spex laser Ramalog system spectrometer showed active modes at 457 cm^{-1} (21.9 μ) and 424 cm^{-1} (23.5 μ), with an intensity ratio of 8:1, which did not appear in the Raman spectrum of sulfur I. A typical Raman pattern is shown in Figure 2 over the range 400–500 cm^{-1}. The active modes, observed consistently, indicate that sulfur XII undergoes a change in polarizability under vibration.

Since we have not as yet been able to synthesize a single crystal of sulfur XII, an infrared study had to be conducted by mixing KBr and sulfur XII to form a polycrystalline pellet and comparing with an ir study of a pure KBr pellet and of a mixture of KBr and sulfur I. The data have not been conclusively interpreted because above about 23 μ the pure KBr pellet sometimes had a somewhat lower or about the same per cent transmittance (52–67%) as the sulfur XII–KBr pellet (50–67%), thus precluding conclusions with respect to bands in sulfur XII above 23 μ. The occasional low transmittance of the KBr pellet was probably due to room and handling conditions. All ir studies were conducted with a Perkin-Elmer 301 unit.

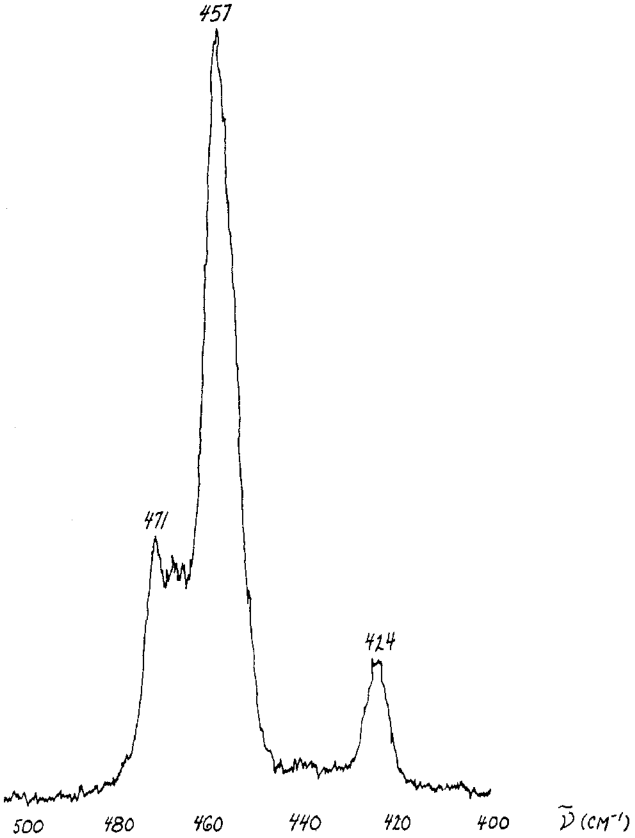

Figure 2.—Laser Raman spectrum from 400 to 500 cm^{-1} of sulfur XII taken 4 months after thermal quenching. The Raman spectrum of sulfur I shows an intense narrow peak at 472 cm^{-1} and a weak peak at 438 cm^{-1}. Therefore, the peaks at 424 and 457 cm^{-1} are clearly associated with sulfur XII.

The sulfur XII infrared patterns taken shortly after quenching and retaken several months later showed an absorption band at 21.9 μ which is also observed in the ir patterns of polycrystalline sulfur I and more intensely at the same wavelength in a single crystal of sulfur I.[21] Despite the high transmittance of sulfur XII above 23 μ, there is some reproducible indication that this phase has an ir absorption band at 23.9 μ which does not appear in the ir of sulfur I. It should be reaffirmed at this point that the sulfur XII samples that were analyzed by Raman and ir spectroscopy showed no trace of sulfur I in careful X-ray examination. The band at 21.9 μ can probably be attributed to the symmetric stretching mode which apparently is the same in both sulfur I and XII. Using a rough diatomic approximation yields a force constant $k = 1.95 \times 10^5$ dyn cm^{-1} which is a reasonable order of magnitude. Since the Raman and ir modes seem to overlap, it is reasonably certain that the sulfur XII molecule cannot be centrosymmetric (possess inversion symmetry) which is in agreement with the "infinite" chain structure.

As mentioned earlier, the structure of sulfur XII belongs to the $P2$ or C_2 point group and has eight ten-atom helical segments per monoclinic unit cell. A C_2 group has two types of vibrations: A and B, singly

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(20) A. Von Hippel, *J. Chem. Phys.*, **16**, 372 (1948).

(21) C. MacNeill, *J. Opt. Soc. Amer.*, **53**, 398 (1963).

degenerate states that are, respectively, symmetric and antisymmetric about the principal axis. Both ir- and Raman-active modes are permitted in state A and state B. A factor group analysis shows that 80 atoms remain invariant under the E operation and four atoms remain invariant under the C_2 operation, giving a reducible representation $\Gamma_R = 240 - 4$. Reducing this according to C_2 gives the total factor group modes n_t for each state A and B: $n_{t(A)} = 118$ and $n_{t(B)} = 122$. This very large number of permissible active modes arises from the high number of sulfur atoms per unit cell of phase XII and the low order of point group C_2.[22]

A site group analysis cannot be performed because the ten-atom helical segment cannot be treated as a polyatomic group such as a sulfate group. Hence the libration and translatory modes cannot be predicted in this manner. The character table for C_2 shows that states A and B allow both an acoustic and a rotation mode. However, no rotation modes occur in crystals. The difference between the total factor group modes and the sum of acoustic, translatory, and libration modes gives the number of internal modes, all of which in the case of C_2 should be active in the ir and in the Raman spectra. Some of these modes may be too weak to observe particularly in polycrystalline ir patterns. However, the Raman spectra over the range of 1–1000 cm^{-1} showed at least 20 absorption modes and indications of several more. Until an infrared study is made on a single crystal of sulfur XII, the group theory analysis cannot be confirmed and the vibrational bands cannot be assigned with confidence. An effort in this laboratory is now under way to grow a large single crystal of sulfur XII hydrostatically.

Although there is evidence that a series of intermediate phases[1,3,4,17] may be involved in the formation of sulfur XII from the starting material sulfur I, data at hand indicate that the net result of the transformation is the unlinking of the puckered rings and the relinking of sulfur atoms in the form of close-packed helical chains in a structure similar to that of selenium and tellurium, displaying one aspect of the progression of polymorphism through group VIa. The reconstructive nature of the phase transformation producing sulfur XII is in agreement with previous studies[3,17] in which it was noticed that the transformation initiated very slowly at the solid–solid boundaries of synthesis and is consistent with a nucleation and growth mechanism as the basis of the phase change. The characterization of the high-pressure phase as a chain-type structure fulfills the prediction of Deaton and Blum[23] that before pressure can induce the transition to a metallic state reported by several workers,[24] it first has to cause a transformation to a chainlike structure.

Properties of Sulfur XII.—*In situ* electrical measurements did not of course give the thermal coefficient of resistance of an equilibrium phase but did show that the formation of sulfur XII (isobarically) is clearly associated with an increasingly negative thermal coefficient of resistance, normally indicative of semiconducting behavior. The slope of the resistance trace became more steeply negative as the temperature was increased above the minimal value of about 240° at which sulfur XII was synthesized at 35 kbars in the study by Vezzoli, *et al.*[1] The resistance decreased most rapidly in the temperature interval from about 375° to the holding temperature of 415° and corresponded to a rough resistivity of about 10^5 ohm-cm at the latter temperature under a pressure of 35 kbars.

From the previous study[3,17] it is known that the polymorphic reaction producing sulfur XII is very rapid at temperatures in excess of about 350°. Thus the temperature *vs.* resistance trace in the present experiment contained contributions from both the kinetic as well as thermal effects. While the experiment was maintained at the holding conditions, the resistance was very sensitive to even small temperature fluctuations (± 2–$5°$) and was constant only when the temperature was constant. Upon cooling to room temperature, the resistance again rose to its initial value at 35 kbars and 20° which corresponded to an approximate resistivity of $\sim 10^8$ ohm-cm. The second heat treatment showed similar resistance characteristics as the first except that the slope changes were less pronounced indicating perhaps that the kinetic effect was providing a smaller contribution and that the bulk of the transformation had taken place during the first heat treatment. As the product was quenched to ambient conditions, the resistance rose almost to its starting value.

The thermally quenched product was a light yellow, very fine-grained material, in agreement with the results of others,[3,5,8] and as mentioned earlier insoluble in CS_2. Although this product has the high resistance characteristic of an insulator, it consistently displays a photoelectric effect characteristic of many semiconductors. Bombardment with ultraviolet light under evacuated conditions at room temperature repeatedly caused the resistance of sulfur XII to decrease immediately by more than an order of magnitude.

Photosensitivity alone does not necessarily affirm semiconducting behavior. However, further evidence that sulfur XII should support conduction better than sulfur I is shown in an electron paramagnetic resonance spectrum of the thermally quenched product. In the puckered-ring configuration, the valence band is completely filled and there are no unpaired electron spins present, and since the electrons are so tightly localized, there is no efficient method to transport an inter-ring current. In sulfur XII the presence of unpaired electron spins is affirmed from epr Varian 4502 spectrometer studies taken of the product several days after quenching and retaken with a different specimen (from the same experiment) 10 months later.

The epr patterns showed slightly asymmetric absorp-

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[22] The fact that multiple twinning exists in Geller's fibrous sulfur as shown from its orthorhombic diffraction symmetry may cause the high-pressure phase to behave under ir and Raman studies somewhat differently from what is ideally predicted by the group theoretical treatment for point group C_2.

[23] B. C. Deaton and F. A. Blum, Jr., *Phys. Rev. A*, **137**, 1131 (1965).

[24] H. David and S. Hamann, *J. Chem. Phys.*, **28**, 1006 (1958); S. Joigneau and J. Thouvenin, *C. R. Acad. Sci.*, **246**, 3422 (1958); J. Berger, S. Joigneau, and G. Bottet, *ibid.*, **250**, 4331 (1960).

tion derivative resonances which are not observed in octameric sulfur I. The g factors of the two samples were 2.0039 ± 0.0005 and 2.0048 ± 0.0005, respectively, and the peak-to-peak line width measured 5.9 G. Since the g factor for sulfur XII is only slightly different from the free electron g factor of 2.0023, spin-only paramagnetism is indicated. No hyperfine splitting of the resonance was observed.

From a comparison with a standard (pitch in KCl) of known stable radical concentration, the epr data indicate that there are about $(1.8 \pm 0.9) \times 10^{17}$ spins/g-atom of sulfur XII, giving a total spin concentration of $(2.0 \pm 1.0) \times 10^{-8}$ g-atom/cm^3. The number of spins in sulfur XII was determined by assuming a Lorentzian-type epr resonance curve and equating the ratio of the numbers of spins to the ratios of equivalent peak amplitudes times the square of the line width.

A similar approach was utilized by Gardner and Fraenkel[25] to study liquid sulfur as a function of temperature and gave a temperature-independent g factor of 2.024 and line widths that generally increased with temperature. By assuming the presence of diradically terminated chains in the liquid state (which has been established by others[26]) and having found a total spin concentration of $(1.1 \pm 0.6) \times 10^{-3}$ M, Gardner and Fraenkel inferred a maximum chain length of $(1.5 \pm 0.7) \times 10^6$ atoms at 171°. This is in good agreement with Gee's[26] report that the maximum chain length is about 10^6 atoms. However, from viscosity data some disparity exists in the measurement of the temperature at which the maximum chain length occurs: 197° according to Gee[26] and 187° according to Bacon and Fanelli.[27] Nonetheless, Eisenberg[11] predicted that the maximum chain length should occur at about 170°.

The above discrepancy may be due to the presence of impurities especially halogens which have been shown by Bacon and Fanelli to reduce viscosity and stabilize chain ends. For this reason, from our measurement of $(1.8 \pm 0.9) \times 10^{17}$ spins in 1 g-atom of sample, no accurate measurement of average chain length can confidently be calculated because we cannot assume that within each grain of sulfur XII every helical chain is terminated diradically. Even in our ultrapure starting material and especially after the pressure and temperature treatment, there are at least 10^{14} impurity atoms in the sulfur XII samples examined by epr and no way of determining just how many chain ends are being obscured from the epr signal by the presence of the impurities and in particular the halogens. The presence of these impurities in fact may account for the rather high dc resistivity of sulfur XII, both in its stable synthesis field and after quenching to ambient conditions. By stabilizing chain ends these impurities may impede the conduction process. We have observed at atmospheric pressure that the resistance of liquid sulfur increases as temperature rises from about 160 to 190° presumably due to the increase in chain length and the accompanying decrease in the number of radicals and chain ends.[28] At temperatures greater than about 190° the resistance decreases as the long chains break up and contribute more radicals and chain ends to the chain concentration of the liquid.[28] It has been suggested to us by Dr. E. H. Poindexter that the rather high dc resistivity of sulfur XII may imply finite chain lengths which can be accounted for by the presence of impurities stabilizing chain ends in the solid state as they do in the liquid.

From a very qualitative correction for impurity content as an estimate of the number of "obscured" chain ends, a tentative indication exists that the average helical chain in our polycrystalline sulfur XII contains about 10^5 atoms. This approximation may be even better than expected because impurities should be preferentially attracted to chain ends while sulfur XII is forming and should distribute themselves randomly over the chains. Thus, statistically the sulfur XII quenched product should be homogeneous with regard to impurity concentration.

Since a ten-atom length along the axis of the helical chain is 13.8 Å,[4] an average length of 10^5 atoms implies that the chain length is of the order of 10 μ and that the ideal helical chain structure of sulfur XII is essentially infinite since the chain length is about equal to the grain size.

Our figure of $(2.0 \pm 1.0) \times 10^{-8}$ g-atom/cm^3 spin concentration is about one-hundredth as great as that found for liquid sulfur at 300° by Gardner and Fraenkel. This is reasonable since the liquid should contain chains of widely varying length, giving rise to considerably more radicals.

The measured g value is typical of free-radical g values. As in most free radicals, the symmetry of sulfur XII (C_2) is so low that the orbital contribution to any spin–orbital coupling is small. The small deviations of ±0.05 or smaller are observed often for most radicals and are thought to be a consequence of mixing of low-lying excited states with the ground state.[29] The average deviation in the g factor of the epr spectrum for sulfur XII is only 0.0020 which is probably too small to warrant extraction of information concerning the nature of the excited states.[30]

Our epr data were repeatedly consistent (four separate runs) and are in good agreement with the work of Sclar, *et al.*,[5] who reported a symmetric peak with a g factor of 2.0036 ± 0.0005 and a width of 5 G for the 4.04-Å phase. In our epr study of a product taken from the center of the sample shortly after quenching, but not treated with CS_2, a broad absorption derivative resonance having a g factor of 2.72 was observed over a sweep of 5 kG. Superimposed upon the spectrum was the approximate free-radical resonance mentioned above plus three additional smaller resonances. The broad resonance, however, was not observed in the sample which was examined 10 months after synthesis

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and had been treated with CS_2 to remove any sulfur I, nor was it observed in the epr pattern of the sulfur I starting material; hence its interpretation is not clear. Broadening of line widths is normally caused by interactions such as spin–spin, spin–lattice, or exchange; however, these mechanisms are not invoked to explain ultrabroad resonances.

From the total epr study it can be concluded that sulfur XII clearly shows the presence of unpaired electron spins which indicates for the s^2p^4 configuration of sulfur that the valence band of sulfur XII is not completely filled in agreement with the band model of semiconductors. Thus a single crystal of sulfur XII should show p-type valence band conduction.

All the characterization data for sulfur XII are summarized in Table II. The results of these experiments suggest that the polymorphic reaction ring sulfur → chain sulfur may be described electrically as an insulator → semiconductor phase transformation. In the ring structure and in the helical chain structure every sulfur atom is bonded covalently to each of its two nearest neighbors. Essentially the same number of electrons are thus used in covalent bonding orbitals in both sulfur I and sulfur XII and since there is no evidence that the transformation itself liberates or delocalizes electrons into conduction bands, the chain structure should also have the high resistance characteristic of a moderately good insulator at room temperature.[31]

TABLE II
SUMMARY AND COMPARISON OF CHARACTERIZATION DATA ON SULFUR I AND SULFUR XII

	Sulfur I	Sulfur XII
Color	Yellow	Yellow
Solubility in CS_2	Very soluble	Insoluble
X-Ray	3.85 Å, strong 3.21 Å, medium 3.44 Å, medium	4.04 Å, strong 3.23 Å, medium 2.90 Å, medium
Structure	Orthorhombic octameric ring	Monoclinic[4,8] (C_2) infinite helical chain
Infrared	21.9 μ	21.9 μ and possibly 23.9 μ
Raman	21.2, 22.8 μ	21.9, 21.2, 23.5 μ
Epr	No detectable resonance	$g_{av} = 2.0045 \pm 0.0005$, $w = 5.9$ G
Photoelectric effect	None detectable	Decrease in resistance by more than an order of magnitude under ultraviolet light
Resistivity	10^{17} ohm-cm at ambient conditions	$\sim 10^5$ ohm-cm at 35 kbars at 415°
Thermal coefficient of resistance	Moderately negative	Very steeply negative

However, when sufficient thermal energy is supplied to drive electrons out of the valence band, then the chain-type structure should show better hole conduction properties than the ring structure. This is because the helical chain structure offers continuity in covalent bonding and thus some electron delocalization in the direction of the helical axis, whereas the ring structure shows this continuity only within each octameric ring.

Conclusions

The X-ray and Raman data show that a severe structural rearrangement resulted from the phase transformation producing sulfur XII. The almost identical correlation between the X-ray powder patterns of Geller's fibrous sulfur and our sulfur XII shows that these phases are the same and hence the latter is based on a helical chain-type structure similar to the structures of the semiconductors selenium and tellurium. The sharp negative thermal coefficient of resistance and the comparatively low resistivity of sulfur XII in its stability pressure–temperature field, as well as observations of the photoelectric effect and unpaired electron spins in the thermally quenched product, indicate that the sulfur XII polymorph may be a semiconductor particularly in its equilibrium p–T field.

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(31) Other factors contributing to the high measured resistance of the quenched product at room conditions were the presence of any unreacted sulfur I, as well as the grain boundaries in polycrystalline sulfur XII which break chain continuity and act as defects causing carrier scattering. Thus a single crystal of sulfur XII should have a lower resistivity.