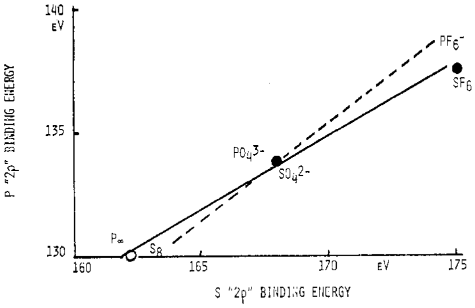

Figure 4.—The "2p" binding energies of phosphorus *vs.* those of sulfur for compounds having the same number, kind, and arrangement of nearest-neighbor atoms (solid points). The open point in this figure corresponds to a structure which is closely related but does not fulfill all of the specifications for the solid points. The solid line goes through the experimental points and the dotted line gives the slope corresponding to the 2p binding energies of various atomic configurations.

tions presented in Table II, the effect of removing a valence-shell electron on the binding energy of the 2p inner-shell electron increases gradually when going from phosphorus to silicon to sulfur. On the other hand, the experimental data indicate that the change in "2p" binding energy by removing a certain amount of valence charge through sharing of electrons with neighboring atoms is about the same for silicon and phosphorus but is considerably greater for sulfur. Both the theoretical and experimental results show an increasing effect with increasing atomic number.

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High-Resolution Photoelectron Spectroscopy of Carbon and Silicon Tetrafluorides[1]

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High-resolution photoelectron spectra of CF_4 and SiF_4 obtained with 584-Å radiation are reported. The spectra are interpreted by relating the photoelectron bands to the energies of the molecular orbitals of the two molecules. Vibrational fine structure observed on the photoelectron bands is assigned to vibrational states of the resulting ions. Evidence of the participation of d orbitals in the bonding of SiF_4 is discussed.

In this paper we report the high-resolution photoelectron spectra of carbon tetrafluoride and silicon tetrafluoride using 584-Å radiation of a helium discharge lamp. Low-resolution spectra of these compounds have been reported[4,5] using the retarding grid type of instrument. These spectra failed to indicate the vibrational fine structure of some of the photoelectron bands which are of considerable help in interpreting the spectra. In this paper we have reexamined the molecular orbital energy level sequences utilizing the additional information available from the high-resolution spectra and suggest new assignments for the molecular orbital sequences in CF_4 and SiF_4. Assignments for the vibrational modes which are excited upon ionization are also discussed.

Discussion

Carbon Tetrafluoride.—The photoelectron spectrum of carbon tetrafluoride consists of three bands (see Figure 1); the first band starts at 15.67 eV, rises smoothly to a maximum intensity at 16.25 eV, and extends into the second smooth band which has a maximum at 17.46 eV. The third band exhibits vibrational fine structure which consists of two series of peaks each with a separation of 0.10–0.11 eV. The first series which has the more intense peaks displays ionization energies of 18.27, 18.37, 18.48, 18.58, 18.69, and 18.80 eV with the maximum intensity of the band coinciding with the 18.58-eV vibrational peak. The second less intense series has maximum intensities at 18.33, 18.44, 18.54, 18.65, 18.76, and 18.87 eV.

Except for our observation of the fine structure on the third band, these data agree very well with the photoelectron spectrum reported by Bassett and Lloyd.[5] Frost, *et al.*,[4] have also reported the photoelectron spectrum of CF_4 and cite vertical ionization energies of 15.9, 17.2, and 18.5 eV. The onset of ionization at 15.67 eV agrees quite well with the recent reports of 15.56,[6]

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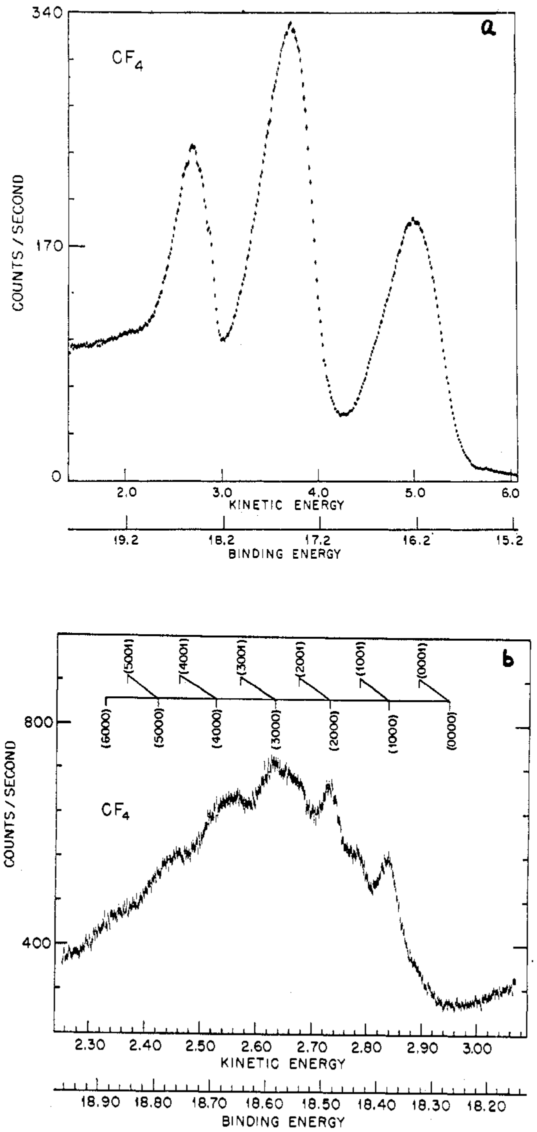

Figure 1.—The photoelectron spectrum of CF$_4$ using 584-Å radiation as a source of excitation. Error bars are given for each point in terms of the square root of the counting rate: (a) total spectrum; (b) the 18.58-eV band showing the vibrational fine structure in detail.

15.52,[7] and 15.35[8] eV for the appearance potential of CF$_3^+$ from CF$_4$ as determined by photoionization studies.

Using the procedure described previously[9] for assessing the relative intensities of the photoelectron bands, we obtained relative intensities of 1.00, 0.98, and (0.33) for the bands at 16.25, 17.46, and 18.58 eV, respectively. The value of the relative intensity for the 18.58-eV band is placed in parentheses since the correction for relative intensities of bands with binding energies of 18.0 eV and greater (electron kinetic energies up to 4.0 eV) becomes as large as or greater than the "corrected" intensity. (The data presented in the figures are not corrected for the intensity variations that accompany measured electron kinetic energy.) Although factors other than degeneracy (*e.g.*, autoionization and photon energy) contribute to the relative intensities of photoelectron bands, these intensities suggest that the first two bands might be of higher degeneracy than the third band. Thus the third band with a vertical ionization energy of 18.58 eV is related to the removal of an electron from the e level. Calculations indicate that the e and t$_1$ orbitals of CF$_4$ are located entirely on the fluorine atoms. At infinite separation of the four fluorine atoms, the e and t$_1$ orbitals are degenerate with a binding energy equal to the ionization energy of the fluorine atom, 17.42 eV.[10] When these four fluorine atoms are near each other, as in tetrahedral CF$_4$, the interaction between the fluorine atoms results in the t$_1$ and e orbitals splitting with the t$_1$ orbitals moving to higher potential energy and the e orbitals moving to lower potential energy. To a first approximation one may view this splitting as occurring around a "center of energy" equal to its value in the fluorine atom. We shall define the calculated "center of energy" as a weighted average by degeneracy of the occupied lone-pair orbitals. Thus, for CF$_4$ it would be three-fifths of the binding energy of the t$_1$ orbitals plus two-fifths the binding energy of the e orbitals. The value of -17.42 eV for the fluorine atom appears to be a lower limit of the calculated "center of energy" in the absence of interaction between orbitals on the central atom and these fluorine orbitals. As empirical evidence for this we list in Table I the binding energies of fluorine-localized electrons in a number of compounds. These data indicate that it is not unusual for the binding energies of these electrons to be as low as 16.0 eV. Even in the case of the F$_2$ molecule, the π_g (antibonding) and π_u (bonding) orbitals give a calculated

TABLE I

BINDING ENERGIES OF F-LOCALIZED ELECTRONS

Compound	Binding energy, eV	Ref
F	17.422	*a*
HF	16.06	*b–d*
F$_2$	15.63 (π_g) 18.46 (π_u)	*b*
CH$_2$F$_2$	15.71 (a$_2$) [g]	*e*
CHF$_3$	16.16 (a) 17.26 (e)	*e, f*
BF$_3$	16.65 (a$_2$) 17.26 (e″)	*h, i*
NF$_3$	~16.3 (a$_2$) 17.44 (e)	*i*

[a] See ref 10. [b] D. C. Frost, C. A. McDowell, and D. A. Vroom, *J. Chem. Phys.*, **46**, 4255 (1967). [c] H. J. Lempka and W. C. Price, *ibid.*, **48**, 1875 (1968). [d] H. J. Lempka, T. C. Passmore, and W. C. Price, *Proc. Roy. Soc.*, *Ser. A*, **304**, 53 (1968). [e] See ref 9. [f] A. D. Baker, Thesis, Imperial College, London, 1958. [g] Assignments of other orbitals are uncertain. [h] R. J. Boyd and D. C. Frost, *Chem. Phys. Lett.*, **1**, 649 (1968). [i] F. A. Grimm, B. P. Pullen, W. E. Bull, W. E. Moddeman, G. K. Schweitzer, and T. A. Carlson, unpublished results.

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"center of energy" of −17.04 eV which is above the lower limit of −17.42 eV. We therefore suggest that the t_1 level of CF_4 lies above the $3t_2$ level, since the assignment of the 16.25-eV vertical ionization energy to the photoelectrons from the t_1 level and the 18.58 eV vertical ionization energy to the e level leads to a "center of energy" of −17.18 eV. Using the assignment of the 17.46-eV vertical ionization energy to the t_1 level gives a "center of energy" of −17.91 eV which is below the lower limit of −17.42 eV. This assignment disagrees with those suggested previously[4,5,11] and also is the reverse of the order obtained by the INDO[4] and CNDO/2[11] semiempirical calculations. However, recent *ab initio* calculations using a Gaussian basis set (11, 7 contracted to 5, 3) have been reported for CF_4 by Gelius.[12] These calculations give the order of the three highest filled orbitals as $t_1 > 3t_2 > e$[12] which agrees with our empirical assignments. The ordering of the energy levels obtained by the semiempirical methods is dependent upon the parametrization[13] and assignments of photoelectron spectra based upon them should be made with caution.

The absence of vibrational fine structure on the first two bands for CF_4 is consistent with the absence of the parent ion, CF_4^+, in photoionization studies.[6–8] The presence of vibrational fine structure on the third band suggests a lifetime of the ^2E electronic state of CF_4^+ greater than the time for a molecular vibration and indicates that this state has a minimum in its potential energy surface.

The values of the ν_1, ν_2, ν_3, and ν_4 vibrational modes of CF_4 are 0.113, 0.054, 0.159, and 0.078 eV,[14] respectively. The vibrational fine structure of the third band consists of two series of equally spaced peaks each with a separation of 0.10–0.11 eV. This separation compares well with the energy of the ν_1 vibrational mode of CF_4. The first series which starts at 18.27 eV is more intense than the second series which starts at 18.33 eV. The two series are separated by 0.06–0.07 eV which is only slightly less than the value of ν_4 of CF_4. The e molecular orbital is C–F nonbonding with the electrons located on the fluorine atoms. It is expected that the CF_4^+ (^2E) ion resulting from the removal of an electron from this orbital would have force constants for stretching vibrations very similar to the force constants of CF_4. The force constants for bending vibrations in the ion might be slightly less than for neutral CF_4. Therefore, the vibrational fine structure of the third band is assigned as indicated in Table II for CF_4 as a tetrahedral molecule (T_d point group).

Finally it is interesting to note that no evidence of splitting of the bands is observed in our spectrum. The two factors which have previously been associated with the observed splitting of photoelectron bands, spin–orbital interactions[15] and the Jahn–Teller effect,[16] are apparently too small in CF_4^+ to be detected. The lack of splitting due to the Jahn–Teller effect is consistent with the calculations of Coulson and Strauss[17] on CF_4^+. These authors found the amount of distortion from T_d symmetry to be very small compared to the distortion of CH_4^+.

TABLE II

IONIZATION ENERGIES OF CF_4

State	Exptl ionization energy, eV		Total rel intens
$2T_1$	15.67[a]		1.0
	16.25[b]		
3^2T_2	17.02[a]		0.98
	17.46[b]		
^2E			
(0, 0, 0, 0)[c]	18.27[a]		(0.33)
(0, 0, 0, 1)		18.33	
(1, 0, 0, 0)	18.37		
(1, 0, 0, 1)		18.44	
(2, 0, 0, 0)	18.48		
(2, 0, 0, 1)		18.54	
(3, 0, 0, 0)	18.58[b]		
(3, 0, 0, 1)		18.65	
(4, 0, 0, 0)	18.69		
(4, 0, 0, 1)		18.76	
(5, 0, 0, 0)	18.80		
(5, 0, 0, 1)		18.87	

[a] Threshold for ionization (upper limit of the adiabatic ionization energy). [b] Vertical ionization energy. [c] The vibrational quantum numbers ν_1, ν_2, ν_3, ν_4, respectively.

Silicon Tetrafluoride.—The photoelectron spectrum of silicon tetrafluoride is shown in Figure 2. The onset of ionization occurs at 15.92 eV. The first band then rises to a maximum at 16.46 eV and extends to about 17.1 eV. The second band starts at 17.16 eV and has its maximum intensity at 17.55 eV. The third band which overlaps the second band has its maximum intensity at 18.09 eV. A fourth band, the only one with vibrational fine structure, starts at 19.13 eV. The first vibrational peak that can be readily discerned is at 19.34 eV. However, inflections on the band can be observed at 19.15, 19.20, and 19.24 eV. A moderately intense series of peaks at 19.15, 19.24, 19.34, 19.43, 19.52, 19.61, and 19.70 eV is observed with the first two of very low intensity. A second series of peaks of less intensity at 19.20, (19.29), 19.38, 19.47, 19.56, 19.65, and 19.74 eV is also observed. The 19.20-eV peak is of very low intensity and the 19.29-eV value is not observable but is estimated to complete the series. The peaks within each of the two series are separated by 0.09–0.10 eV. These data along with the relative intensities of the four bands are given in Table III.

These data agree with the results of Bassett and Lloyd;[5] however, these workers did not observe the vibrational fine structure of the fourth band. Herron

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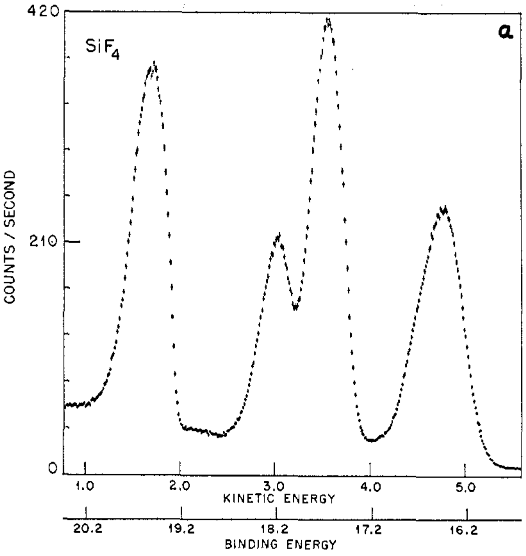

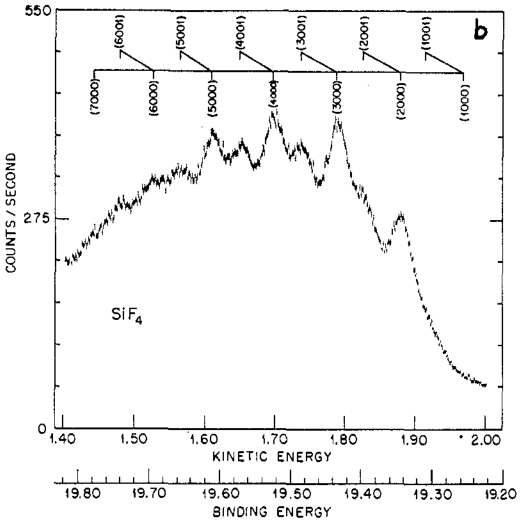

Figure 2.—The photoelectron spectrum of SiF_4 using 584-Å radiation as a source of excitation. Error bars are given for each point in terms of the square root of the counting rate: (a) total spectrum; (b) the 19.52-eV band showing the vibrational fine structure. Lower vibrational states, presumably (0, 0, 0, 0) and (0, 0, 0, 1), were discernible in a trace obtained at a wider sweep.

and Dibeler[18] reported an appearance potential of 15.4 eV for SiF_4^+ by electron-impact mass spectroscopy. No computed values for the energy levels in SiF_4 could be found in the literature.

The similarity of the vibrational structure of the fourth band in the SiF_4 spectrum and the third band of CF_4 is immediately apparent. The values of the ν_1, ν_2, ν_3, and ν_4 vibrational modes[19] of SiF_4 are 0.099, 0.026, 0.128, and 0.048 eV, respectively. The separation of 0.09–0.10 eV occurring in each of the two series of vibrational peaks on the fourth band of SiF_4 is assigned to the ν_1 vibrational mode of SiF_4^+. The two series are separated by 0.04–0.05 eV. This separation is believed to correspond to the excitation of the ν_4 vibrational mode of SiF_4^+. The very similar vibrational fine structure of the third band of CF_4 (IP = 18.58 eV) and the fourth band of SiF_4 (IP = 19.52 eV) lead us to consider that these ionization potentials correspond to the removal of an electron from molecular orbitals of the same symmetry, namely, the e molecular orbitals.

TABLE III

IONIZATION ENERGIES OF SiF_4

State	Exptl ionization energy, eV		Rel total intens
$2T_1$	15.19[a]		1.00
	16.46[b]		
4^2T_2	17.16[a]		0.93[c]
	17.55[b]		
4^2A_1	18.09[b]		(0.35)[c]
^2E			
(0, 0, 0, 0)[d]	19.15[a]		(0.42)
(0, 0, 0, 1)		19.20	
(1, 0, 0, 0)	19.24		
(1, 0, 0, 1)		(19.29)	
(2, 0, 0, 0)	19.34		
(2, 0, 0, 1)		19.38	
(3, 0, 0, 0)	19.43		
(3, 0, 0, 1)		19.47	
(4, 0, 0, 0)	19.52[b]		
(4, 0, 0, 1)		19.56	
(5, 0, 0, 0)	19.61		
(5, 0, 0, 1)		19.65	
(6, 0, 0, 0)	19.70		
(6, 0, 0, 1)		19.75	
(7, 0, 0, 0)	19.78		

[a] Threshold for ionization (upper limit of the adiabatic ionization energy). [b] Vertical ionization energy. [c] Due to overlap of bands these values of the relative intensities are uncertain. [d] The vibrational quantum numbers ν_1, ν_2, ν_3, ν_4, respectively.

The lower potential energy of this level in SiF_4 as compared to CF_4 (−19.52 *vs.* −18.58 eV) is expected if the d orbitals of silicon are involved in the bonding of SiF_4. CNDO/2 calculations for SiF_4 in which the d orbitals of silicon were included result in the molecular orbital sequence $1t_1 > 4t_2 > 3t_2 \approx 4a_1$ e while similar calculations which excluded the d orbitals gave the order $4t_2 > 1t_1 > e > 4a_1 \approx 3t_2$ (see Table IV). Thus the e molecular orbital is stabilized upon the inclusion of the d orbitals. Although our calculations probably overemphasize the effect of the d orbitals, the results do show that the ordering of the energy levels can change in situations in which d orbitals participate in the bonding. Our calculations indicate that the $4a_1$, e, and $3t_2$ levels have energies such that they might be observed in our spectrum. However, because the calculated energies depend on the parametrization, we prefer not to assign these levels on the basis of these calculations alone.

TABLE IV

CNDO/2-CALCULATED ORBITAL ENERGIES FOR SiF_4

Orbital	Energies including d orbitals,[a] eV	Energies without d orbitals, eV	Orbital	Energies including d orbitals,[a] eV	Energies without d orbitals, eV
t_1	19.92	19.21	$4a_1$	23.33	21.44
$4t_2$	21.28	17.62	e	23.94	19.54
$3t_2$	23.30	21.69			

[a] A Slater exponent of 1.96 was used for the d orbitals.

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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.

[20] We thank one of the reviewers for calling this point to our attention.

CONTRIBUTION FROM THE INSTITUTE FOR EXPLORATORY RESEARCH,
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The Ring → Chain High-Pressure Polymorphic Transformation in Sulfur and the Accompanying Change from Insulating to Modest Semiconducting Behavior

BY GARY C. VEZZOLI* AND ROBERT J. ZETO

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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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