

spectra could be found by comparison with Ar⁺-sputtered carbon-free spectra.

⁸The oxygen signal from the SiO₂ substrate could easily be separated from any oxygen contamination of (SN)_x by the different charging characteristics of SiO₂ and (SN)_x.

⁹D. E. Parry and J. M. Thomas, *J. Phys. C: Solid State Phys.* **8**, L45 (1975).

¹⁰W. I. Friesen, A. J. Berlinsky, B. Bergersen, L. Weiler, and T. M. Rice, private communication.

¹¹U. Gelins, in *Electron Spectroscopy*, edited by D. A. Shirley (North-Holland, Amsterdam, 1973), p. 311.

¹²A. A. Bright *et al.*, *Phys. Rev. Lett.* **34**, 206 (1975).

¹³A deconvolution of peak 4 and shoulder 5 into two peaks was performed assuming zero overlap between the peaks and an intensity ratio of 2:1. This underestimates somewhat the intensity of peak 5 because of the higher cross section of S 3*p* derived orbitals (see Ref. 11). Both assumptions tend to give a conservative estimate for the width of peak 5.

¹⁴L. Pintschovius, H. P. Geserich, and W. Möller, *Solid State Commun.* **17**, 477 (1975).

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Orthogonalized-Plane-Wave Band Structure of Polymeric Sulfur Nitride, (SN)_x

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We present the first orthogonalized-plane-wave band structures and corresponding densities of states for two reported crystal structures of polymeric sulfur nitride, (SN)_x, and compare our results with experiment. We examine the band structures in light of the low-temperature stability of the metallic and superconducting states in (SN)_x and conclude that this stability derives from closed Fermi surfaces introduced by electronic interchain coupling.

Understanding the physical properties of metallic polymeric sulfur nitride, (SN)_x, is presently an actively sought objective of several research groups. Although highly anisotropic in its conductivity,¹ (SN)_x does not undergo a Peierls-Fröhlich transition to an insulating state at low temperatures, but rather continuously increases in conductivity and indeed becomes superconducting at 0.3°K.² At least three hypotheses can be presented to explain this behavior. (1) Incommensurabilities exist between the various Fermi vectors and the reciprocal-lattice vectors which tend to suppress the Peierls-Fröhlich transition.³ (2) Following Klemm and Gutfreund,⁴ the nature of the interpolymer coupling in (SN)_x may be such as to favor stabilization of the superconducting state at temperatures higher than the Peierls-Fröhlich state. (3) (SN)_x is really not one-dimensional, and sufficient dimensionality exists in the Fermi surface to exclude Peierls-Fröhlich distortions except for possible fluctuation effects.

In order to explore these alternatives, we have performed the first orthogonalized-plane-wave (OPW) calculations on (SN)_x.⁵ We present here the band structures and one-electron densities of states resulting from the two reported crystal structures. We also compare our findings with data deriving from x-ray-photoemission spec-

troscopy (XPS),⁶ specific-heat,⁷ and optical measurements.^{8,9} The first structure determination was made by Boudeulle¹⁰ (Lyon structure) based on electron-diffraction studies. Recently, a new structure has been put forward by Mikulski *et al.*¹¹ (Penn structure) using x-ray-diffraction techniques. Other non-OPW calculations exist for the Lyon structure¹²⁻¹⁸; however, we present the first three-dimensional band structure of any kind which directly compares results obtained for both the Lyon and Penn structures within the same computational technique.¹⁹ The two structures possess the same space group, C_{2h}⁵, and have nearly the same monoclinic unit-cell parameters and, in fact, do not differ greatly in bond angles and distances along the polymer chain. However, the degree of interchain coupling may be considerably different because of larger sulfur-sulfur spacing (3.47 Å) in the Penn structure as compared to the Lyon value (3.10 Å). We shall show how this difference affects each band structure.

The resulting OPW bands for the Lyon and Penn sulfur-nitrogen atomic positions are given in Figs. 1 and 2, respectively, along with an inset of the Brillouin zone labeling the various symmetry points in *k* space. At Γ a fundamental basis set of 187 OPW's, extended by perturbation

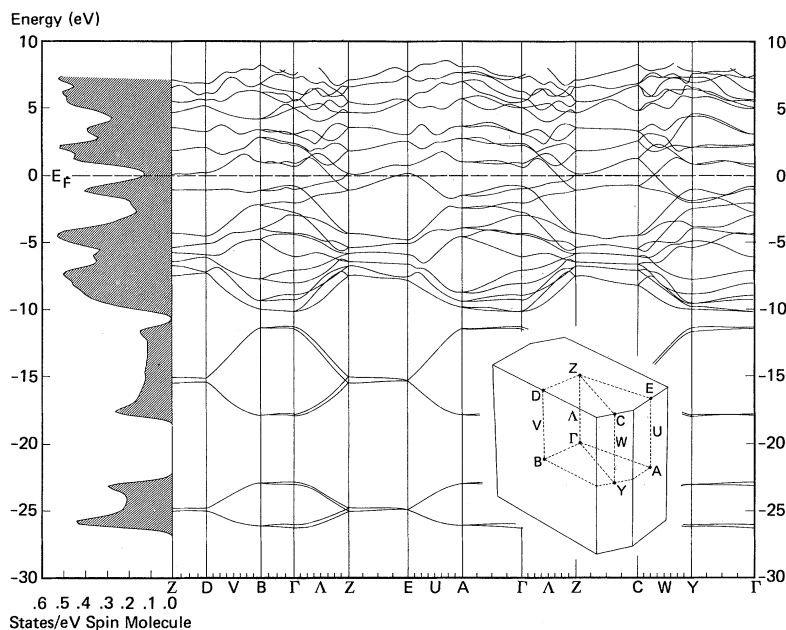


FIG. 1. OPW energy bands for $(\text{SN})_x$, Lyon structure. The density-of-states curve on the left was obtained by placing a Gaussian function with half-width equal to 0.25 eV on each energy level and summing over the 128 points sampled in the Brillouin zone. The zone itself is shown in the inset. The energy scale was chosen to put the Fermi level at zero.

to a total of 550 OPW's, was employed. The crystal potential was created by superposing sulfur and nitrogen atomic potentials, which were in turn computed using the Kohn-Sham statistical exchange model.²⁰ Use of Slater exchange²⁷

broadened the bands somewhat and lowered the lowest core level by about 2 eV. Here we report the Kohn-Sham results exclusively. The calculation was nonrelativistic and non-self-consistent.²² Convergence was tested by doubling the basis set

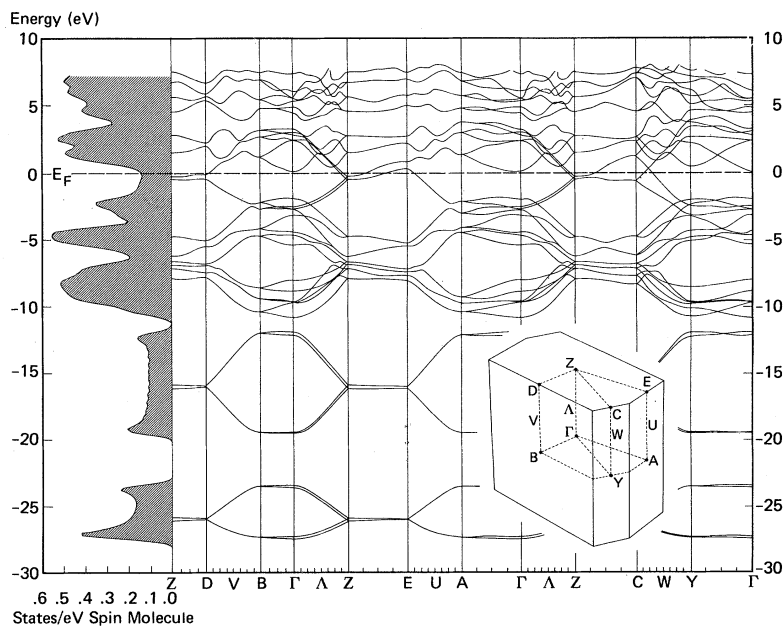


FIG. 2. OPW energy bands for $(\text{SN})_x$, Penn structure. The density of states was obtained as for Fig. 1.

which resulted in narrowing the core-level bands. Convergence near the Fermi level was satisfactory. The Fermi level was located by the histogram method, the Brillouin zone being subdivided into 128 sectors and then filled with the appropriate number (44) of electrons.

Contact with previous tight-binding calculations^{12,13} can be made by observing the behavior of our bands along the line $\Gamma\Lambda Z$ for either structure in the vicinity of the Fermi level. We find the characteristic zone-boundary degeneracy at Z in addition to band crossings occurring along Λ near Z . Because of an extra degeneracy due to time reversal, the bands along the lines U and V are doubly degenerate. Bands in these directions possess essentially one symmetry label and hence may not cross. However, bands along Λ and W do not have such extra degeneracies, and crossings are permitted for bands with different symmetry labels, there being two such labels in each of these directions. All points on the top surface of the zone (plane $ZDCE$) are doubly degenerate. We note the cumulative conduction-band width to be about 2–3 eV. This value is in good agreement with tight-binding estimates derived from recent optical data⁸ in addition to those obtained from previous specific-heat measurements.⁷ The earlier optical measurements of Bright *et al.*⁹ originally suggested much smaller bandwidths.

The effects of interchain coupling may be most clearly seen at the Z point, especially around the Fermi level, as was evident in earlier calculations and from simple physical arguments.^{12,13} Note that there is a marked change in the relative Z -point splitting depending on the crystal structure chosen, being roughly 1.0 eV for the Lyon result and 0.3 eV for the Penn parameters, and that the nature of the electron pocket along Λ is quite different. Also, the depth of the hole pocket at E is affected. For neither structure do we observe the formation of an electron pocket near Γ as found by Kamimura *et al.*,¹⁴ and Schlüter, Chelikowsky, and Cohen,¹⁷ although one nearly appears for the Penn structure. We observe that the Fermi vectors defining the electron- and hole-pocket boundaries in the directions parallel to the chain axis have no special commensurate relationship to the intrachain reciprocal-lattice vector. Therefore, the likelihood of a distortion occurring to remove all degeneracies simultaneously is very small. This incommensurability is a consequence of symmetry, hybridization, and interchain coupling as

can be seen from a study of the bands for both structures.

The degree of band dispersion in the interchain directions is not greatly different for the two structures, ZE and ZD serving as examples, being of the order of an electron-volt in the widest case. Interestingly, some bands, such as ΓA and ΓB near 1.0 eV, are wider in the Penn structure than in the Lyon despite the greater sulfur-sulfur distance. We remark that bands in the interchain directions in $(SN)_x$ are, on the whole, more dispersive than bands in the intrastack direction in the conducting tetracyanoquinodimethane salts.²³ As pointed out by Klemm and Gutfreund,⁴ interchain coupling by electron transfer would favor stabilization of the superconducting state in a quasi one-dimensional system. We feel $(SN)_x$ has sufficient interchain dispersion to permit this mechanism to operate.

Work on the hole and electron Fermi surfaces for both $(SN)_x$ structures is in progress. Details are as yet incomplete, but several overall features emerge from observing the Fermi level intersections with the bands shown in Figs. 1 and 2. In each case, and for both holes and electrons, the Fermi surfaces are closed. For the Penn structure, the electron pockets intersect the zone-boundary plane $ZDCE$ forming closed multiply connected surfaces. Thus we find, contrary to the results of Schlüter, Chelikowsky, and Cohen,¹⁷ that the Fermi surfaces in $(SN)_x$ are not warped parallel sheets, as would be the case for weak interchain interaction, and we believe this discovery constitutes the principal reason why $(SN)_x$ is stable against Peierls-Fröhlich effects.²⁴

The most notable difference in the one-electron density of states given in Figs. 1 and 2 involves a shift of the first peak found below the Fermi level. We see from the band diagram that this shift arises from a depression of the bands, most clearly seen along the intrachain direction DVB , from roughly -1.0 eV in the Lyon structure to about -2.0 eV for the Penn result. Thus, there appears to be little evidence that the degree of interchain band dispersion, shown above to be important in determining Fermi surface topology, affects greatly the density of states which is by and large formed from the intrachain bands. Agreement with existing XPS measurements is good; however, the data are not sufficient to determine which crystal structure is appropriate.⁶ Magnitudes of the Fermi-level density of states are found to be near 0.13

states/(eV spin molecule) for both structures. This is in reasonable agreement with specific-heat results corrected for electron-phonon interaction.⁷

In conclusion, we have computed from first principles, by the OPW method, the electronic energy bands and density of states curves for the two presently proposed crystal structures. In terms of our original hypotheses for the stability of the metallic and superconducting states in $(\text{SN})_x$, both structures satisfy requirements for incommensurability, interchain transfer, and Fermi-surface dimensionality. However, we believe our results show that it is this last factor which is of overall importance in $(\text{SN})_x$. It is quite difficult to visualize a three-dimensional distortion which would split all the degeneracies of a closed nonpolygonal Fermi surface. We therefore offer the following guideline: A quasi one-dimensional system is defined, within the confines of one-electron band theory, as one whose Fermi surfaces consist of warped sheets which do not touch or come close within the first Brillouin zone. Experiment suggests^{9,8,2} and OPW calculations confirm that $(\text{SN})_x$ cannot be termed quasi one-dimensional within the framework of this definition.

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²²Although our calculation does not achieve self-consistency, it appears from a recent SN molecular computation (D. R. Salahub and R. P. Messmer, to be published) that only 0.5 electron is transferred from sulfur to nitrogen, a result confirmed by XPS studies (Ref. 6). Moreover, cluster calculations on SN chain groups (W. E. Rudge, to be published) and the work of Salahub and Messmer both indicate $3d$ hybridization on sulfur to be less than 10% in any of the molecular orbitals. Thus we feel the inherent limitations of the OPW method in representing d -electron effects are not a major factor for $(\text{SN})_x$.

²³Berlinsky, Carolan, and Weiler, Ref. 19.

²⁴Recently, M. J. Cohen, A. F. Garito, A. J. Heeger, A. G. MacDiarmid, C. M. Mikulski, and M. S. Saran (to be published), and R. H. Baughman, R. R. Chance, and M. J. Cohen (to be published), have discussed the frequent occurrence of (100) twinning in $(\text{SN})_x$. This effect was also pointed out in the thesis of Boudeulle (Ref. 10). Calculations on semiconductor polymorphs suggest that the major features of a band structure are formed from nearest- and next-nearest-neighbor inter-

actions [see, for example, I. B. Ortenburger, W. E. Rudge, and F. Herman, *J. Non-Cryst. Solids* **8-10**, 653 (1972)]. We believe our cluster calculations show

this to be the case for $(\text{SN})_x$ also and that our principal conclusions are valid even in the presence of twin activity.

X-Ray-Photoelectron-Spectroscopy Determination of the Valence Band Structure of Polymeric Sulfur Nitride, $(\text{SN})_x$

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We report x-ray photoemission (XPS) measurements on polymeric sulfur nitride, $(\text{SN})_x$. Both valence-band states and core-level binding energies have been studied. The charge transfer δ in the $\text{S}^{+\delta}\text{N}^{-\delta}$ bond is estimated to be 0.30–0.42 electrons. The XPS spectra are compared with densities of states derived from a single-chain tight-binding calculation and also with three-dimensional orthogonal-plane-wave (OPW) calculations based on the two reported $(\text{SN})_x$ crystal structures. Good quantitative agreement is found with the OPW density of states.

The inorganic complex polymeric sulfur nitride, $(\text{SN})_x$, exhibits unusual properties which have provoked considerable interest. This compound has been shown in a variety of experimental studies to be a highly anisotropic metal¹⁻⁴ above 0.3 K and a superconductor⁵ below. An important question in this material is the degree to which a given physical property is dominated by the one-dimensional characteristics of the $(\text{SN})_x$ chain structure. In this paper we examine experimentally the one-electron valence-band density of states of $(\text{SN})_x$ by x-ray-photoemission (XPS) techniques and, by comparison with band-structure calculations, deduce the effect of dimensionality on this quantity.

The XPS data for $(\text{SN})_x$ were obtained on a Hewlett-Packard 5950 A ESCA spectrometer. X-ray monochromatization ($\text{Al } K \alpha$, 1486.6 eV) and dispersion compensation yielded an 0.8-eV full width at half-maximum resolution for the $\text{C}(1s)$ line. Nonoriented $(\text{SN})_x$ films were prepared on gold substrates. The method of preparation was similar to that described for $(\text{SN})_x$ crystals by Street *et al.*⁶ The films were transported in air to the XPS apparatus and electrically grounded to the instrument to avoid surface charging. The sample temperature was controlled at $(298 \pm 3)^\circ\text{K}$ and measurements performed in a vacuum maintained at 1×10^{-9} Torr. Care was taken in preparation to avoid contamination by oxygen and car-

bon. In our best samples, the intensity ratio of the $\text{N}(1s)$ to the contaminant $\text{O}(1s)$ lines was 9:1 and 5:1, respectively. In homogeneous $(\text{SN})_x$ films of thickness 1–2 μm no contribution from the substrate was observed. Table I shows the nitrogen and sulfur core-level energies in freshly prepared samples. We noted a dependence of the sulfur p -level spin-orbit splitting (normally 1 eV) on exposure time to air or the x-ray beam. After long exposure, the splitting disappeared completely, a fact we attribute to gradual oxidation of surface sulfur.⁷ Area analysis of the $\text{N}(1s)$ and $\text{S}(2p)$ peaks yielded a value of 1.02 for the S-to-N ratio based on reported standard intensities.⁸

Siegbahn⁹ has found an experimental relation-

TABLE I. XPS-determined core-level energies of sulfur and nitrogen in $(\text{SN})_x$.

Element	Level	Binding energy (eV)
N	$1S_{1/2}$	-397.3
S	$2S_{1/2}$	-228.5
	$2P_{3/2}$	-163.5
	$2P_{1/2}$	-164.5
	$2P^a$	-164.5

^aAfter long exposure (>4 h) to air or the XPS x-ray beam.