

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.

ship between the binding energy and net charge as determined by the chemical shifts of the S(2p) and N(1s) lines in several nitrogen- and sulfur-containing compounds. Applying his criteria to our core-level data on $(\text{SN})_x$, we obtain a charge transfer figure of +0.31 electrons for sulfur, and, independently, -0.42 for nitrogen. We believe the difference to lie within experimental uncertainties. Recently, Salahub and Messmer¹⁰ have calculated the charge transfer for an isolated SN molecule by the self-consistent-field- $X\alpha$ -standing-wave method and obtained $\text{S}^{+0.5}\text{N}^{-0.5}$ in reasonable agreement with our XPS values.

The XPS spectrum for the valence-band region is shown in Fig. 1. The Fermi level was referenced to the $4F_{7/2}$ binding energy of Au at 83.95 eV. The energy distribution curve extends about 30 eV below E_F and shows a small but finite magnitude at E_F . At present, we are unable to associate this magnitude definitely with a finite density of states at the Fermi level. We note that Grobman *et al.* obtained zero energy-distribution magnitudes at E_F in both the ultraviolet photoemission (UPS) and XPS spectra of TTF TCNQ (tetrathiafulvalene tetracyanoquinodimethane), where localization effects are thought to predominate.¹² It is possible such may be the case for $(\text{SN})_x$ as well, inasmuch as our preliminary UPS measurements yield almost negligible signal in the vicinity of the Fermi level.¹³ On the other hand, the orthogonalized-plane-wave (OPW) calculations do predict that the Fermi-energy density of states should be quite small. The raw XPS spectrum was corrected for background inelastic-scattering contributions using estimates found from the core levels as described by Fadley and Shirley¹¹ and the corrected curve is also shown in the upper half of Fig. 1. Six distinct peaks or shoulders are observed.¹⁴ In the lower half of Fig. 1 we show the single-particle electron density of states (DOS) obtained from two different band-structure calculations. A one-dimensional tight-binding (1DTB) computation has been published by Parry and Thomas¹⁵ using empirical extended Hückel methods and recently a three-dimensional OPW (3DOPW) calculation was done by Rudge and Grant.¹⁶ The 1DTB result is based on a planar model for a single $(\text{SN})_x$ chain, whereas the 3DOPW calculation was performed for the two reported three-dimensional crystal structures of $(\text{SN})_x$.^{17,18} Only the Lyon-structure density of states is given in Fig. 1. Although the qualitative agreement of the corrected XPS data with the 1DTB DOS

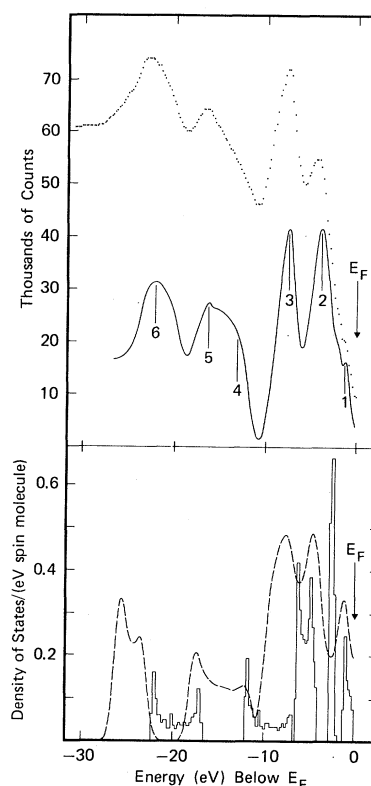


FIG. 1. Top: X-ray photoemission spectrum, raw data (dotted line) and background-corrected by the method of Ref. 11 (solid line). Bottom: One-electron valence-band density of states for a one-dimensional planar chain (1DTB, solid line), and for a three-dimensional OPW calculation based on the Lyon crystal structure (3DOPW, broken line). The ordinate scale refers only to the OPW result which was obtained using an 0.25-eV Gaussian broadening function.

is reasonably good, much better quantitative correlation is obtained for the 3DOPW DOS, especially in the position of the states below peak 1. The agreement in peak intensity between 3DOPW and experiment is also quite good if we assume an energy-independent photoionization cross section to exist. The correlation in peak position between 3DOPW and XPS is poorest for peak 6 and we might suspect that the OPW basis set is insufficient for such a deep valence band. In fact, when the number of OPW's was doubled, the agreement between the 3DOPW DOS and peak 6 was noticeably better. On the other hand, the DOS near E_F remained relatively unchanged. The measured intensity of peak 1, just below E_F , is considerably lower than predicted by either DOS curve. This is probably due to a combination of poor XPS resolution and incomplete knowledge of

exactly how to treat the background correction in these low-energy regions exhibiting greatest sensitivity to such factors.

We now discuss the role of interchain coupling in determining the XPS spectrum. Recently, a new crystal structure for $(\text{SN})_x$ has been proposed by Mikulski *et al.*¹⁸ (Penn structure). This structure, deriving from x-ray-diffraction rather than electron-diffraction measurements, is presumably more accurate than the Lyon structure. Of immediate interest to us is the larger interchain, nearest-neighbor, sulfur-sulfur distance for the Penn structure which implies a different degree of interchain band dispersion, i.e., bandwidths, than results from the Lyon structure. Thus, a comparison of the valence-band DOS calculated from both the Lyon and Penn structures, in addition to the 1DTB DOS of Parry and Thomas, with the corrected XPS spectrum should afford a qualitative estimate of the effects of interchain coupling in determining the $(\text{SN})_x$ valence-band density of states. Figure 1 gives the 3DOPW DOS for the Lyon structure and the 1DTB DOS of Parry and Thomas; the corresponding 3DOPW DOS for the Penn structure may be found in Ref. 16. Although the overall 3DOPW DOS remains remarkably unchanged, despite the changes in sulfur-sulfur distance, there is observed a 0.8-eV shift of peak 1 to lower energies for the Penn structure. In Ref. 16 it is shown that this shift arises from a displacement of certain intrachain bands and is not a direct consequence of interchain band dispersion. *None of the DOS structure appears directly related to interchain bands.* Thus, one can only expect XPS data to reflect the effect of interchain coupling through shifts of the intrachain bands, from which the DOS predominantly arises, and to be relatively insensitive to interchain band dispersion. This latter quantity, of course, determines interchain transport and optical properties and bears directly on the question of quasi one dimensionality in $(\text{SN})_x$.¹⁶ Finally, our view of the relatively inactive role of interchain coupling in the XPS of $(\text{SN})_x$ is reinforced by the general agreement of our data with the 1DTB DOS. Insofar as using XPS spectra and OPW valence-band densities of states to differentiate between the two extant crystal structures is concerned, we presently find better agreement with the Lyon structure even though the Penn structure may be more accurate. However, further discussion of this point should await more definitive results for the density of states near E_F which we are currently obtaining via UPS

studies, together with a more detailed understanding of the OPW convergence properties near E_F .

In summary, our results show clearly the metallic behavior of $(\text{SN})_x$ by virtue of a small electron yield observed at the Fermi level. From an analysis of the core-level spectra, we estimate the amount of charge transfer in $(\text{SN})_x$ to be about 0.30–0.42 of an electron from sulfur to nitrogen. By comparing experiment with theoretical calculations one finds good qualitative agreement with 1DTB DOS and good quantitative agreement with 3DOPW DOS. Moreover, comparison of the XPS spectra with the 3DOPW DOS determined from two crystal structures with differing amounts of interchain coupling leads us to conclude that the XPS structure is dominated by the band dispersion along the chains and not that between them.

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Focused Intense Ion Beams Using Self-Pinched Relativistic Electron Beams

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A new two-dimensional diode simulation code is used to show the possibility of using hemispherical diodes to produce converging ion beams in the 1–10-MA range. The pinched electron flow enhances ion emission, while suppressing electron emission, allowing $I_i/I_e > 1$. Such focused ion beams are of considerable interest for use in ablatively driven implosions of fusion targets.

Ion currents of up to 10 kA have been produced in the reflex-triode work of Humphries, Lee, Sudan, and Condit.¹ It has been predicted by Creedon, Smith, Prono, and Bergstrom that a reflex triode with a fractional-range foil anode can produce still larger ion current densities.² However, substantial applied magnetic fields are required, and are not compatible with spherical implosions. Another method for generating large ion currents is to use a diode in which the electrons are insulated from the anode using an externally applied magnetic field in plane or cylindrical geometry.³ The theory of both reflex triodes and magnetically insulated diodes has been discussed by Antonsen and Ott.⁴ In this paper we discuss a third method for obtaining large ion currents which does not employ an external field, can be 50–75% efficient, and provides for spherical ion focusing. Previously we showed that the electric field of a pinching electron beam may itself be used to produce ion beams of hundreds of kiloamperes in cylindrically symmetric planar diodes.⁵ The idea is that the electrons flow radially inward between the electrodes, displacing the equipotentials towards the anode (the largest displacement occurs at the axis of symmetry, as in the parapotential model⁶); the resulting higher electric field at the anode causes enhanced ion emission (assuming an ion source, i.e., anode

plasma, is present). This shifting of equipotentials also causes reduced emission of electrons from the cathode, making it possible in some cases for the ion current to exceed the electron current (and thus using most of the input energy to accelerate ions, rather than electrons).

The problem in using ion beams from planar anodes for pellet implosion studies is that the ions form a rather parallel beam, whereas one would like a focused ion beam. Thus we have examined this problem in spherical geometry, and this paper will make plausible the possibility of producing reasonably well-focused ion beams (i.e., focused to dimensions < 1 cm) in the megampere regime.

For this study, a new particle simulation code was written, the spherical counterpart of the previously described cylindrical code.^{5,7} The code is two-dimensional (r, θ with φ the symmetry coordinate), and both electrons and ions are treated self-consistently. The device consists of two identical hemispheres with the target at their center; the top half of such a hemisphere is shown in Fig. 1. The cathode is inside the anode so the ions move radially inwards. The electrons pinch to the axis of symmetry (at the pole of the hemisphere). A thin anode plasma is required to provide a source of ions, but plays no other role in the electron pinch. The case shown