Paul Grant

PROPERTIES OF POLYSULFURNITRIDE — THE FIRST SUPERCONDUCTING POLYMER

B. H. SCHECHTMAN, * W. D. GILL, P. M. GRANT, R. L. GREENE, P. MENGEL, W. E. RUDGE and G. B. STREET

IBM Research Laboratory
San Jose, California 95193

(With 6 text-figures)

The polymers discussed at this Symposium, and in fact most polymers known today, generally have high electrical resistivity at room temperature which increases further as the temperature is lowered. Furthermore, such polymers often form solids which are structurally amorphous or highly disordered collections of microcrystals.

In the last two years, experimental studies of the inorganic polymer sulfur nitride, $(SN)_x$, have shown that this material represents quite an exception to conventional polymer behavior. In the form of macroscopically oriented crystals $(SN)_x$ exhibits the properties of a highly anisotropic metal with a resistivity which decreases with decreasing temperature and which vanishes at a superconducting transition near 0.3°K. This represents the first case of a quasi-one-dimensional material which shows intrinsic metallic behavior at all temperatures, as well as the first report of superconductivity in a polymer. As such, there is considerable interest in achieving fundamental understanding of the electronic properties in this system in order to gain further insight into the problem of designing other polymeric metals and superconductors with desirable properties, e.g., higher superconducting transition temperatures.

In this paper we review recent work in the preparation and characterization of $(SN)_x$. Experimental results on electrical, thermal and spectroscopic properties, in addition to electronic structure calculations, lead to our present understanding of $(SN)_x$ as a highly anisotropic metal.

Polysufurnitride has been known for over 60 years but it has only been in the last few years that highly crystalline samples have been prepared [1, 2] and the structure of $(SN)_x$ determined [3]. It is now established that the sulfur and nitrogen atoms alternate in covalently bonded chains which are separated in the crystal by distances large compared to the intrachain bonds. The structure is illustrated by a side view of the chains shown in Fig. 1, although some debate exists as to the exact positions of the atoms [4].

$(SN)_x$ is formed by the solid state polymerization of S_2N_2 which is obtained by heating S_4N_4 in vacuum. Recent improvements [2] in the growth technique have permitted formation of crystals in the shape of needles up to 10 mm long with transverse

* Present address, IBM Corporation, Armonk, New York 10504.

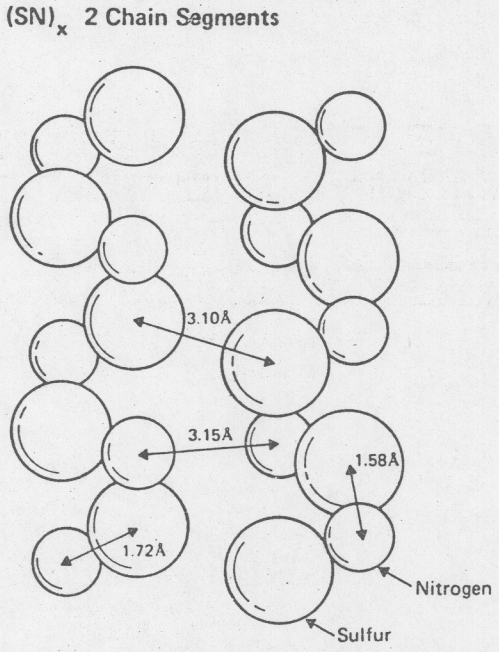


Fig. 1. Projection of the $(SN)_x$ structure on the (102) crystal plane.

dimensions of up to 0.5 mm, as well as more equidimensional samples with faces several mm [2]. There has also been progress in growing oriented films of $(SN)_x$ on several organic substrates, which provide even larger area samples [5].

Although $(SN)_x$ crystals have been well characterized using chemical analysis, x-ray diffraction and other physical tools, they thus far lack some of the characterization that one has come to expect for well characterized organic polymers. For example, no imformation has yet been obtained on the distribution of chain lengths in the crystals, owing to the lack of a non-destructive solvent for $(SN)_x$. The strongest physical evidence for the polymeric nature of these crystals is the extreme ease of cleavage along planes parallel to the chain axis. This results in a microstructure of the crystals, when viewed by scanning electron microscopy, which consists of large numbers of parallel fibres, the smallest of which are less than 2000 A in diameter [2].

In addition to making the structural characterization of $(SN)_x$ possible, the availability of large crystalline samples has allowed the first quantitative studies of the anisotropy of this compound, both electrically and optically. The electrical data is summarized in Fig. 2. The resistivity parallel to the polymer chains decreases monotonically with temperature over the entire range below 300°K, in contrast to the linear chain and organic charge transfer conductors, which show semiconducting or insulating regimes at low temperature. A parallel resistivity minimum between 20 and 30°K reported in early studies [1] is absent from the high quality crystals, and is attributed to defects in the early samples. Furthermore, we find a direct correlation between better crystal quality, lower values of room temperature resistivity and higher ratios between room temperature

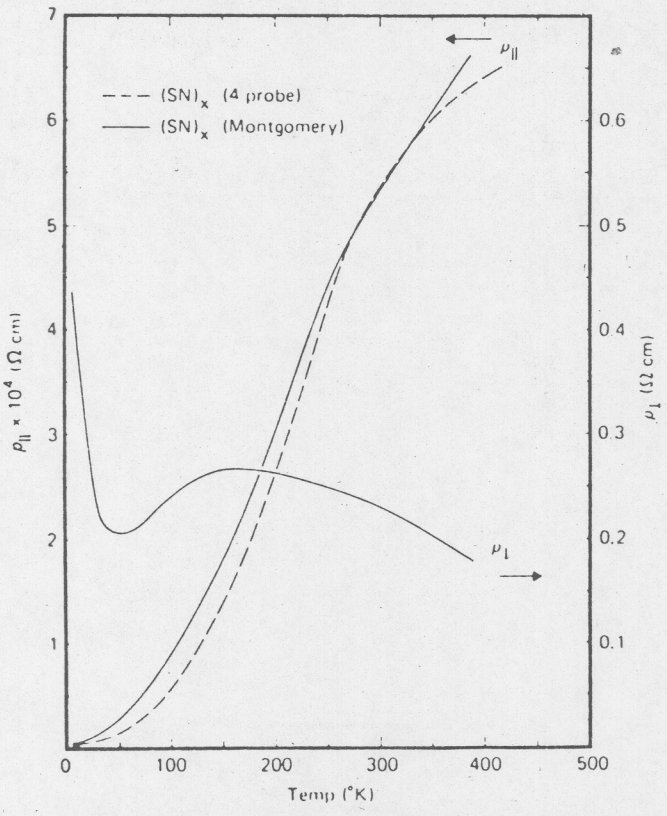


Fig. 2. Electrical resistivity of $(SN)_x$ crystal as a function of temperature

and low temperature resistivity, clearly indicating that even in our best samples the conductivity may be defect limited. Our Montgomery probe measurements of transverse resistivity indicate a large anisotropy ratio; however, the values of may be artificially large because of the fibrous microcrystals, and the intrinsic anisotropy ratio of $(SN)_x$ remains open to question.

Optical measurements on single crystals of $(SN)_x$ are perhaps a better probe of the intrinsic anisotropy since the excitation samples regions of the crystal which are small compared to the distance between defects. The polarized reflectivity of an $(SN)_x$ crystal is shown in Fig. 3. Here the anisotropy is quite pronounced, with Drude-like metallic behavior for polarization parallel to the chain axis, and a considerably less metallic response for the transverse polarization. Analysis [6] of the parallel data leads to an intrachain bandwidth of about 2.5 eV, which suggests that electron delocalization along the chains is much greater than in conventional molecular solids, perhaps more comparable to the delocalization in the d-bands of transition metals.

Additional support for fairly delocalized electron states near the fermi energy in $(SN)_x$ comes from the low temperature specific heat data shown in Fig. 4. Analysis of the linear portion of this data gives a lower limit on the bandwidth of about 1 eV [7].

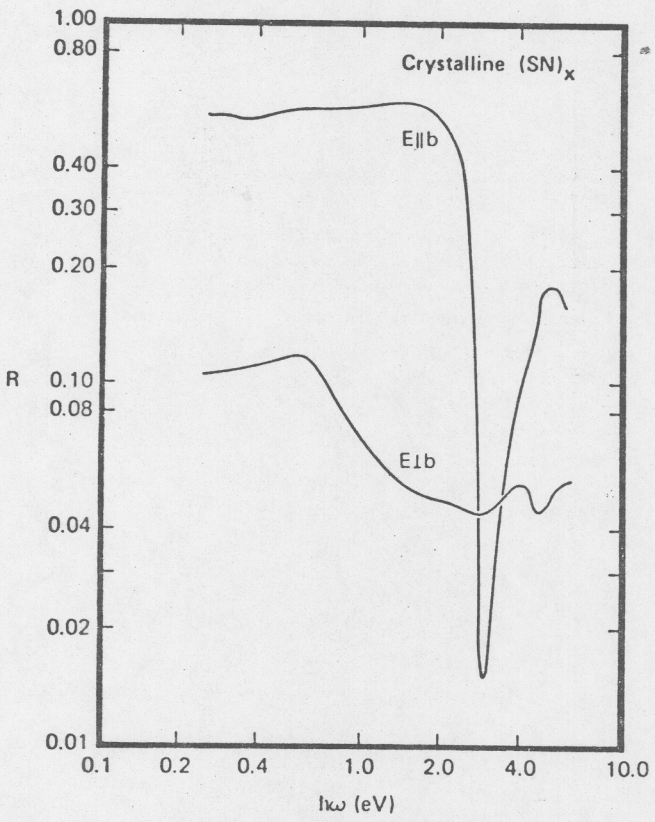
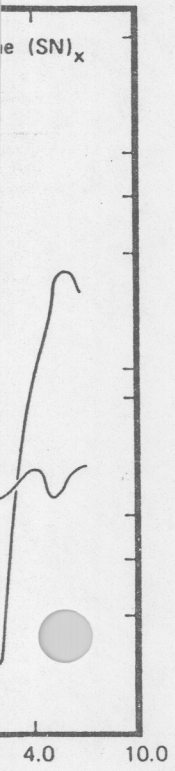


Fig. 3. Polarized reflectance spectra of $(SN)_x$ crystals at 300°K.

An interesting feature of the specific heat studies at higher temperatures (up to 77°K) is the departure of the lattice contribution from the conventional T^3 dependence, which for organic polymers has been an indication of chain bending contributions to the heat capacity.

The electronic structure of $(SN)_x$ has been examined by x-ray photoelectron spectroscopy (XPS) and by several theoretical models. The densities of occupied states derived from two models are shown in Fig. 5, along with preliminary XPS data in the valence band region. The two models approach the $(SN)_x$ electronic structure from opposite extremes. One, the OPW band calculation, emphasizes the full three dimensional structure and takes account of all interchain interactions. The other calculation, a self-consistent-field scattered wave treatment, models $(SN)_x$ in terms of a cluster of atoms constituting one isolated chain. Both calculations agree quite well in a qualitative way with the overall valence band width and the major structural features seen in the XPS data. The OPW energy bands in k-space [8] show relatively weak interchain dispersion in the nearest neighbor interchain directions (along the sulfur-sulfur directions) and intrachain bandwidths near the fermi level of 1 to 2 eV, quite consistent with the analysis from the optical and thermal experiments. On the other hand, the success of the cluster model



als at 300°K.

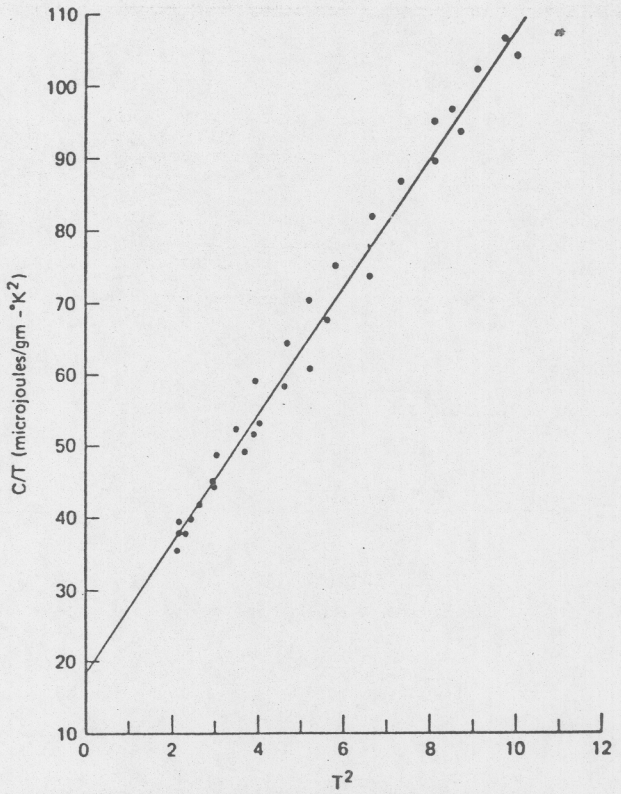


Fig. 4. Low temperature heat capacity of $(SN)_x$.

temperatures (up to 77°K) is
al T^3 dependence, which for
g contributions to the heat

ned by x-ray photoelectron
densities of occupied states
preliminary XPS data in the
$)_x$ electronic structure from
zes the full three dimensional
The other calculation, a self-
terms of a cluster of atoms
ite well in a qualitative way
eatures seen in the XPS data.
interchain dispersion in the
ur directions) and intrachain
nt with the analysis from the
success of the cluster model

emphasizes the dominant role in the electronic structure played by the intrachain bonds, and will provide a vehicle for future work to quantitatively treat intrachain interactions by modelling sets of several $(SN)_x$ chains.

The superconducting transition [9] in $(SN)_x$ near 0.3°K is illustrated in Fig. 6, which shows the parallel resistance as a function of temperature with and without an applied transverse magnetic field. The relatively broad transition region may be associated with defects or disorder in the samples. It has been found that higher quality crystals have somewhat higher transition temperatures and narrower transitions [2]. The electronic anisotropy persists even below the transition, as evidenced by anisotropy in the critical magnetic field data [10]. The occurrence of superconductivity in $(SN)_x$ has been independently confirmed in several laboratories, and the transition has been seen in specific heat as well as in electrical measurements [11].

The unique low temperature behavior of $(SN)_x$ among quasi-one-dimensional solids raises the question of why this compound alone does not distort into a Peierl's insulator but instead remains metallic and ultimately becomes superconducting. A speculative response to this question is that, although $(SN)_x$ is highly anisotropic, interchain interactions play a major role in stabilizing its metallic state. Recent experiments support

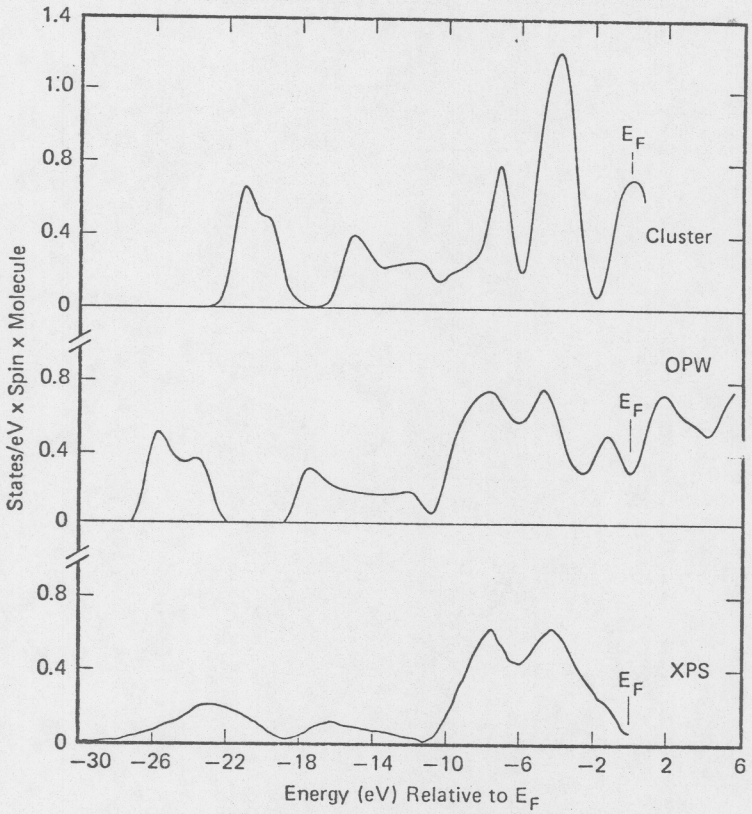


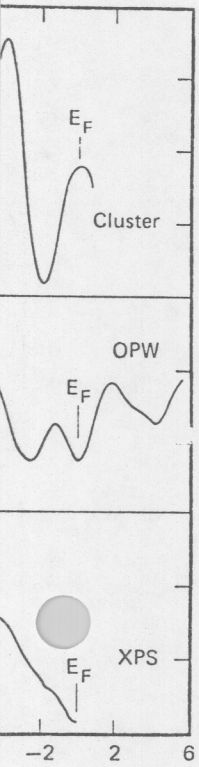
Fig. 5. Theorical and experimental valence band spectra for $(SN)_x$.

the idea that interchain interactions are important, since they show that the superconducting transition occurs at the same temperature for the transverse and parallel crystal directions, and that increasing the interchain interaction with hydrostatic pressure significantly increases the transition temperature [12].

In summary, polysulfur nitride has been shown to be a quasi-one-dimensional metal with an anisotropy that is evidenced in all its physical properties. A quantitative understanding is still required of the balance between this compound's polymeric (i.e., one dimensional) nature and the influence of interchain (three dimensional) interactions. With this understanding, it should be possible to construct other compounds related to $(SN)_x$ with even more interesting and desirable properties.

ABSTRACT

Recently it has been possible using slow solid state polymerization to produce high quality large single crystals of the inorganic polymer of sulfur nitride, $(SN)_x$. Unlike the cyclic sulfur nitride structures S_4N_4 and S_2N_2, which form insulating molecular crystals, $(SN)_x$ is a metal at all temperatures below 300°K. As such it represents the first



a for $(SN)_x$.

hey show that the super-
the transverse and parallel
n with hydrostatic pressure

uasi-one-dimensional metal
properties. A quantitative
ompound's polymeric (i.e.,
dimensional) interactions.
ther compounds related to

merization to produce high
nitride, $(SN)_x$. Unlike the
sulating molecular crystals,
ich it represents the first

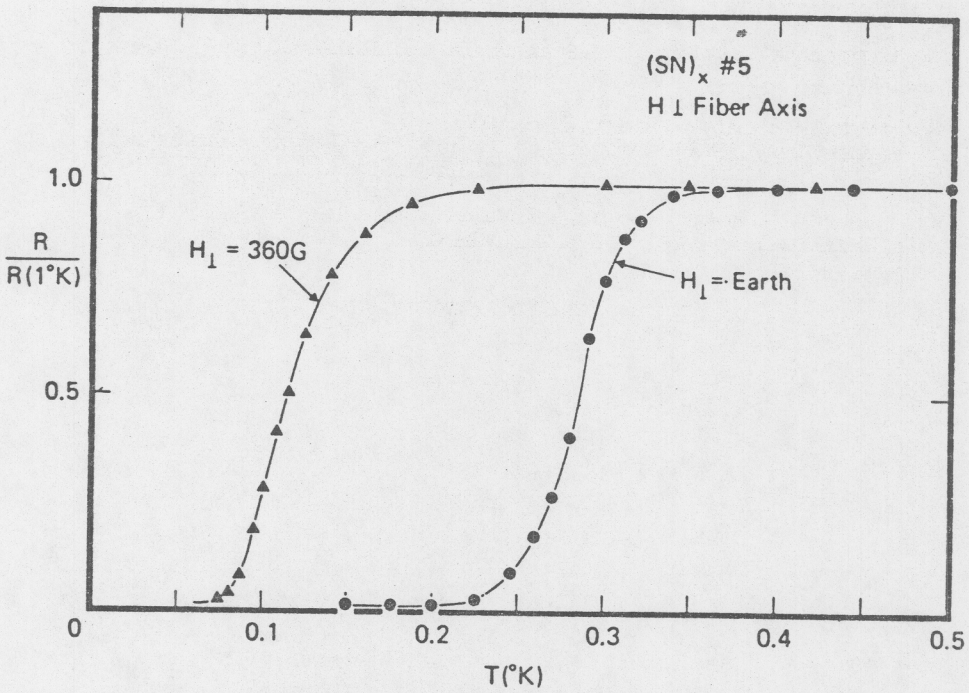


Fig. 6. Superconducting transition in $(SN)_x$ showing the effect of a transverse magnetic field.

quasi-one-dimensional system which does not undergo a distortion to an insulating state upon cooling. Recently, it has been found that $(SN)_x$ becomes superconducting at 0.3°K, which is the first occurrence of this phenomenon in a polymer or in any material composed of only elements from the "insulating" region of the periodic table.

Results will be reported on the electrical conductivity, heat capacity and optical properties of $(SN)_x$, including studies of the anisotropy of this solid. The superconducting transition has been characterized by four-probe conductivity recorded in the Montgomery configuration, by measurement of the critical magnetic fields parallel and perpendicular to the polymer chain, and by studies of the influence of hydrostatic pressure on the transition temperature and width. The unusual properties of this polymer metal will be discussed and interpreted using the results of electronic structure calculations based on both an OPW band model and on cluster models of the molecular chains.

REFERENCES

1. V. V. WALATKA, M. M. LABES and J. H. PERLSTEIN, Phys. Rev. Lett. *31*, 1139 (1973); C. HSU and M. M. LABES, J. Chem. Phys. *61*, 4640 (1974).
2. G. B. STREET, H. ARNAL, W. D. GILL, P. M. GRANT and R. L. GREENE, Nat. Research Bull, (Sept. 1975).

3. M. BOUDEULLE, Ph. D. Thesis, Univ. of Lyon (1974); M. BOUDEULLE, Cryst. Struct. Comm. *4*, 9 (1975).
4. C. M. MIKULSKI, P. J. RUSSO, M. S. SARAN, A. G. MACDIARMID, A. F. GARITO and A. J. HEEGER, J. Am. Chem. Soc. (to be published).
5. A. A. BRIGHT, M. J. COHEN, A. F. GARITO, A. J. HEEGER, C. M. MIKULSKI and A. G. MACDIARMID, Appl. Phys. Lett. *26*, 612 (1975).
6. P. M. GRANT, R. L. GREENE and G. B. STREET, Phys. Rev. Lett. (to be published).
7. R. L. GREENE, P. M. GRANT and G. B. STREET, Phys. Rev. Lett. *34*, 89 (1975).
8. W. E. RUDGE and P. M. GRANT (to be published).
9. R. L. GREENE, G. B. STREET and L. J. SUTER, Phys. Rev. Lett. *34*, 577 (1975).
10. L. J. AZEVEDO, W. G. CLARK, R. L. GREENE, G. B. STREET and L. J. SUTER (to be published).
11. L. F. LOU and R. POHL (private communication).
12. W. D. GILL, R. L. GREENE, G. B. STREET and W. A. LITTLE (to be published).

international symposium on electrets and dielectrics

Honoring the 70th Birthday
of Prof. Bernhard Gross

simpósio internacional sobre eletretos e dielétricos

Homenageando o 70º Aniversário
do Prof. Bernhard Gross

ORGANIZED BY:

Instituto de Física e Química de São Carlos,
Universidade de São Paulo
Caixa Postal – 369
13560 – São Carlos, SP, Brasil

ORGANIZING COMMITTEE:

Sergio Mascarenhas
Guilherme Fontes Leal Ferreira
Milton Soares de Campos

SPONSORS:

Academia Brasileira de Ciências
Fundação de Amparo à Pesquisa do Estado de São Paulo
Conselho Nacional de Desenvolvimento Científico e Tecnológico

EDITOR:

Milton Soares de Campos

ndo [illegible]cional
cnológico (FNDCT)
Projetos S.A. (FINEP).