Molecular Crystals and Liquid Crystals

Comparison of the Physical Properties of Polysulfur Nitride, $(SN)_x$, to Related Organic Polymer Systems and (TTF) (TCNQ)

P. M. Grant [a], R. L. Greene [a], W. D. Gill [a], W. E. Rudge [a] & G. B. Street [a]

[a] IBM Research Laboratory, San Jose, California, 95193, U.S.A.
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Comparison of the Physical Properties of Polysulfur Nitride, (SN)$_x$, to Related Organic Polymer Systems and (TTF) (TCNQ)

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

IBM Research Laboratory, San Jose, California 95193 U.S.A.

Much attention is currently being directed toward the experimental and theoretical study of conducting quasi-one-dimensional systems, of which (TTF) (TCNQ) and KPC (K$_2$Pt(CN)$_4$Br$_{0.3}$ · 3.2H$_2$O)[1] are the principal prototypes. All of the known materials derived from these prototypes either undergo a metal-insulator transition at some finite temperature, or become several times more resistive at low temperatures than at room temperature; furthermore, all known organic polymer systems are insulators at all temperatures. By contrast, the highly anisotropic conducting polymer polysulfur nitride, (SN)$_x$, not only becomes continuously less resistive with decreasing temperature, but in fact is a superconductor below 0.3°K.[2] It is important to understand why quasi-one-dimensional instabilities are suppressed in (SN)$_x$ thus allowing superconductivity to occur. Such knowledge may serve as a guide in synthesizing new organic metals stable to much lower temperatures.

We report here measurements of the normal conductivity, superconductivity, optical reflectivity and specific heat of crystalline (SN)$_x$ along with electronic band structure calculations based on the crystal structure determined by Boudeulle.[3] The (SN)$_x$ crystals were grown by the solid state polymerization of S$_2$N$_2$ crystals which were in turn grown from the vapor of sublimed S$_4$N$_4$ passed through silver wool. Morphologically, the resulting crystals exhibit a characteristic fibrousness when examined by scanning electron microscopy. The width of the thinnest observable fibers is estimated to be between 1600–2000 Å. The fibers are believed to separate along the

cleavage planes identified by Boudeulle,[3] a fact which constitutes the strongest direct evidence of extreme anisotropy or quasi-one-dimensionality in $(SN)_x$.

The normal state conductivity of $(SN)_x$ is summarized in Figure 1.[4] Note that the resistivity parallel to the fibers decreases with temperature and does not pass through a minimum as do all conducting TCNQ salts and KPC. On the other hand, the temperature dependence of $\rho_{\parallel}$ appears more complex than for simple metals. The resistivity perpendicular to the fibers, $\rho_{\perp}$, differs from $\rho_{\parallel}$ by roughly 10 or greater over most of the low temperature range and displays a resistivity minimum in the region of 40°K. Because of the fibrousness of all samples measured to date, the extent to which our data reflects the intrinsic $\rho_{\perp}$ is still open and under investigation.
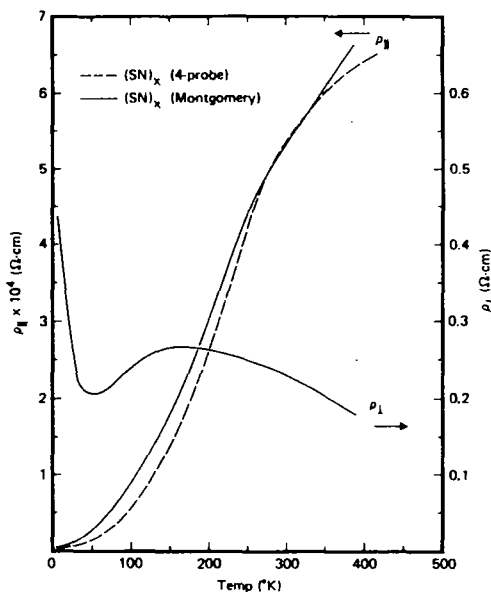

FIGURE 1   Crystalline $(SN)_x$ resistivity parallel and perpendicular to the fiber axis (b-axis).

A somewhat more direct picture of the electronic anisotropy is given in Figure 2 which shows the polarized optical reflectance of an $(SN)_x$ crystal. Here we observe a definite Drude-like behavior for light polarized along the fibers (b-axis of the $(SN)_x$ monoclinic unit cell), whereas, for $E \perp b$, the rise in reflectivity is considerably less dramatic and it is questionable whether it is of metallic origin. Nonetheless, this slight rise does not occur in the transverse spectrum of (TTF) (TCNQ)[5] and it is reasonable to attribute its presence in $(SN)_x$ to a greater amount of electronic interchain coupling than in the former compound. Drude–Lorentz fitting procedures applied to the
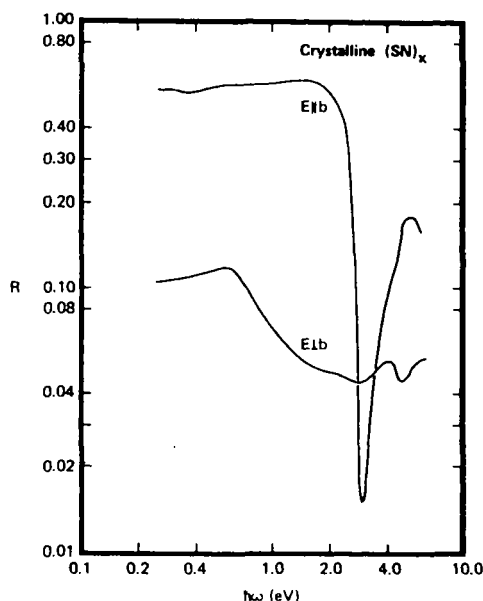
FIGURE 2   Polarized reflectance of crystalline $(SN)_x$ with respect to the b-axis of the unit cell.

$E \parallel b$ data result in values of 4.6 eV for the plasma energy and 1.0×10^{-15} sec for the Drude lifetime. From the plasma energy and carrier concentration $(3.05 \times 10^{22}$ cc$^{-1})$ we obtain a value for the reduced hole-electron effective mass of 2. In (TTF) (TCNQ)[5] m^* is about 5, implying greater band dispersion for $(SN)_x$. In the sense of a half-filled tight-binding band, we would deduce the intrachain bandwidth to be 2.5 eV.

This conclusion is supported by an analysis of the low temperature specific heat[6] of $(SN)_x$ shown in Figure 3. From the linear portion of the C/T vs. T^2 fit, we obtain a value of $D(\varepsilon_F) = 0.18$ states/eV spin molecule for the Fermi surface energy density of states which yields a tight-binding bandwidth of ~ 1 eV; however, the inclusion of electron–phonon coupling into the analysis of $D(\varepsilon_F)$ would increase the estimate of the bandwidth toward the optical result. Evidence of anisotropy in the lattice dynamics of $(SN)_x$ is provided by observing in Figure 3 the departure of the specific heat at higher temperatures from a T^3 dependence. As discussed elsewhere,[6] $(SN)_x$ is similar to organic polymers in this regard.

At 0.3°K, $(SN)_x$ becomes superconducting and exhibits an anisotropic critical magnetic field dependence similar to that observed in the layered transition metal dichalcogenides. At this time, we believe the superconductivity to be of the usual BCS type involving pair formation via electron–phonon interaction. One must ask, in view of the marked electronic aniso-
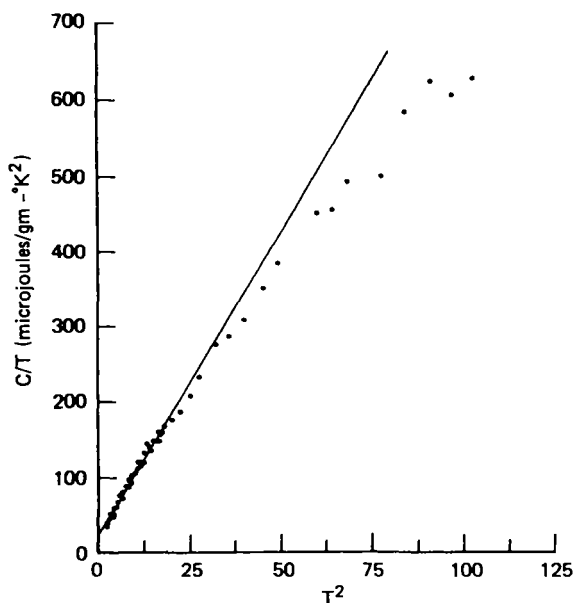
FIGURE 3   Specific heat of $(SN)_x$ between 1.5 and 10°K. The solid straight line shows the fit below 3.2°K.

tropy in $(SN)_x$, why the material does not undergo a Peierls transition before becoming superconducting. It is well known that phase transitions do not stabilize from the fluctuation regime in purely one-dimensional systems except at $T = 0°$K. Recently, it has been shown that interchain coupling by electron tunneling[7] can lead to finite temperature singlet superconductivity in quasi-one-dimensional materials. This idea is especially suggestive for $(SN)_x$ given the less than van der Waals distance between sulfur atoms on neighboring polymer chains.[3] A possible reason for the suppression of the Peierls transition in $(SN)_x$ can be seen by noting the location of the electron pocket in the conduction band of the OPW band structure shown in Figure 4. Given the relatively weak dispersion in the nearest neighbor interchain directions, one might expect the Fermi surfaces containing the electron pocket to approximate flat and parallel sheets throughout the Brillouin zone. As the Fermi vectors defining the surfaces need have no special commensurate relationship with either each other or the reciprocal lattice vector in the chain direction, the period of the lattice distortion necessary to lift both Fermi degeneracies may have to extend over many unit cells and thus may never stabilize. The creation of the electron pocket is due to a combination of $(SN)_x$ unit cell symmetry and asymmetries in band dispersion caused by molecular orbital hybridization or interchain overlap. The most
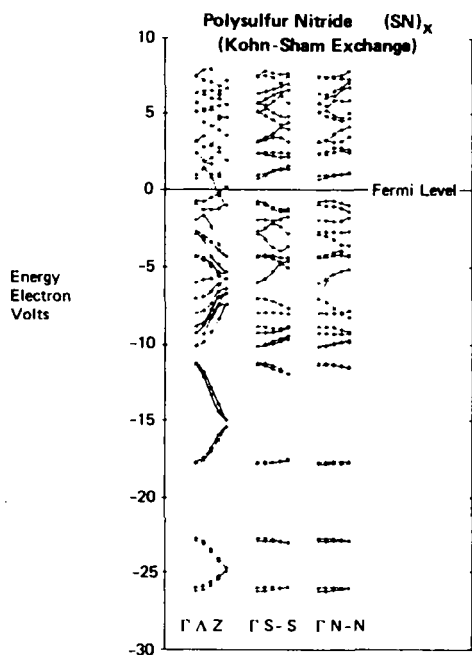
FIGURE 4 OPW band structure of $(SN)_x$ along selected direction in the Brillouin zone. $\Gamma\Lambda Z$ is the line from the zone center to the zone boundary in the chain direction. $\Gamma N-N$ and $\Gamma S-S$ are lines from the zone center to the zone boundary in the nearest neighbor interchain nitrogen and sulfur directions, respectively.

important unit cell symmetry factor is a 180° screw rotation along the chain axis without which $(SN)_x$ would be nominally an insulator since there are four electrons per unit cell. This symmetry operation permits four-fold degeneracies (spin included) to exist at Z, which, in the presence of interchain wavefunction overlap are moved back along Λ and weakly split. Asymmetries in band dispersion pin the Fermi level as shown in Figure 4 thus creating the electron pocket and, in addition, a corresponding hole pocket elsewhere in the Brillouin zone. Hence, in this picture, $(SN)_x$ is seen to be a semimetal.

It is interesting to note that a similar screw axis symmetry also exists in the uniform bond length interpretation of the structure of polyene. However, polyene, unlike $(SN)_x$, is insulating, a property believed to derive either from coulomb correlation (Mott–Hubbard state) or through bond alternation (Peierls state).[8] If the latter assertion is correct, the bond length and angle alternation between CH groups must destroy any screw axis symmetry otherwise polyene would be semimetallic.

In summary, our work on $(SN)_x$ suggests that attempts to synthesize organic conducting polymer systems, stable to low temperatures, should concentrate on enhancing interchain interaction. Also, one should be aware that even electron chain systems, normally expected to be insulating, may exhibit semimetallic properties analogous to $(SN)_x$, given similar symmetries internal to the unit cell.

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