

There are three parameters in Eq. (2) which determine the behavior of the model and these can, within limits, be determined without reference to surface order. We took  $J_2/J_1$  as  $-0.2$ , quite close to the preferred value of  $-0.25$  suggested in Ref. 7. To illustrate best the contrast between results from the bulk and from the surface, we adjusted  $J_1$  so that the calculated points for the bulk order parameter agree with experiment<sup>4</sup> up to the experimental transformation temperature. This gave  $J_1/k = 237^\circ\text{K}$ , a value about 7% higher than would have been obtained by the procedure of Ref. 7. Finally we let  $\Delta E = 2.5J_1$ , corresponding to a constant average surface composition.

In Fig. 4 we show the average of the order parameters for the two topmost Cu-Au layers, for the two boundary conditions of the surface model, together with the measured surface order and the calculated bulk order as a function of temperature. It appears from the figure that the difference between the observed behavior of the long-range order parameter at the surface and that in the bulk can be explained by a simple model involving only nearest- and next-nearest-neighbor interactions which are the same for both surface and bulk. Furthermore, it is evident from the analysis that consideration of a region of accommodation between surface and bulk is a necessary

feature of any model meant to describe the phenomenon of long-range order at a crystal surface.

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## Polysulfur Nitride—a One-Dimensional Chain with a Metallic Ground State

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The temperature dependence of the electrical conductivity and Seebeck coefficient for the polymer chain system  $(\text{SN})_x$  has been measured along the chain axis from 4.2 to 300°K. The data show the system to be metallic over the entire temperature range studied, with a small conductivity maximum at  $\sim 33^\circ\text{K}$ .

Considerable interest exists in examining the properties of both organic and inorganic structures which are highly anisotropic and can be visualized as containing one-dimensional chains—metallic “spines”—surrounded by a matrix whose properties are highly important in determining the transport properties of that system. The or-

ganic and inorganic systems of interest have, in the main, been the highly conducting charge-transfer salts of tetracyanoquinodimethane (TCNQ)<sup>1</sup> and the mixed-valence Pt chain complexes.<sup>2</sup> However, these compounds show “metal-insulator” transitions at temperatures varying from 60 to 250°K which have been interpreted in terms of

one of three effects: (a) a Peierls instability along the one-dimensional chain<sup>3</sup>; (b) a Mott transition<sup>4</sup>; or (c) phonon-assisted variable-range hopping due to disorder<sup>5</sup> or finite chain length<sup>6</sup> which becomes diffusive at high temperatures. The observation of extraordinary conductivity maxima in the charge-transfer salt of tetrathiofulvalene (TTF) with TCNQ<sup>7a</sup> in a few crystals out of many measured, with the typical crystal<sup>7</sup> displaying a weaker conductivity maximum, has added to the interest in achieving highly conducting ordered one-dimensional arrays with a metallic ground state.

Conceptually, a polymeric strand which is a conjugated structure fulfills the requirements of being a one-dimensional metal in which the "breaks" in the metallic strands might be very few, particularly if high molecular weights could be achieved. For most polymers, however, the extent of electron delocalization within the chain is very small.<sup>8</sup> An exception to this is the polymer polysulfur nitride,  $(\text{SN})_x$ , which has been known since 1910,<sup>9</sup> but whose chemistry was elucidated in the 1950's by Goehring.<sup>10</sup> Investigation on this system has never been very popular because one of the intermediates is explosive. Recently, however, further information about its crystal structure<sup>11</sup> and experimental considerations minimizing the danger of explosion<sup>12</sup> prompted us to reinvestigate its properties.<sup>13</sup> Although the study is far from complete, preliminary results indicate the polymer itself to behave like a metal over the entire temperature range from 4.2 to 300°K, and to show a very weak conductivity maximum at 33°K when measurements are performed along the chain axis.

The structure of the polymer was originally described<sup>10,14</sup> as a resonance hybrid with equivalent bond lengths between all sulfur and nitrogen atoms. However, a recent electron-diffraction analysis indicates  $(\text{SN})_x$  to have the following structure<sup>11a</sup>:



with alternating S-N bond lengths of 1.55 and 1.73 Å (theoretical for S=N, 1.54 Å, and for S-N, 1.74 Å) and bond angles as indicated. "Crystals" are monoclinic with a gold- or brass-colored metallic luster.

$(\text{SN})_x$  was synthesized and crystals grown in the following manner<sup>12,15</sup>:  $\text{S}_4\text{N}_4$  was sublimed *in vacuo* through silver wool heated to 473°K; if the

collecting cold finger was kept at 193°K, then  $\text{S}_2\text{N}_2$ , a white explosive solid, was obtained. If the cold finger was maintained at 273°K, shiny bronze-colored "crystals" of  $(\text{SN})_x$  were formed, which were washed with benzene and ether to remove any unpolymerized  $\text{S}_2\text{N}_2$ . These "crystals" were composed of bundles of parallel fibers and measurements were performed by cutting out bundles of these fibers 2 mm long with a cross section of  $\sim 0.3 \times 0.2 \text{ mm}^2$ . Chemical analysis shows a 1:1 atomic ratio of S to N, but the samples also contain 0.13% C, 0.42% H, and 4.93% O by weight. Semiquantitative emission spectrographic analysis did not detect the presence of any metal impurities at the parts per million level.

Measurements were performed using a crystal mounting procedure and a low-temperature electrical conductivity and Seebeck apparatus described elsewhere.<sup>16</sup> All data reported are for measurements along the chain axis using the four-probe technique for the conductivity measurements.

Large variations in conductivity from crystal to crystal, probably reflecting crystal defects and breaks in the  $(\text{SN})_x$  fibers, were encountered.

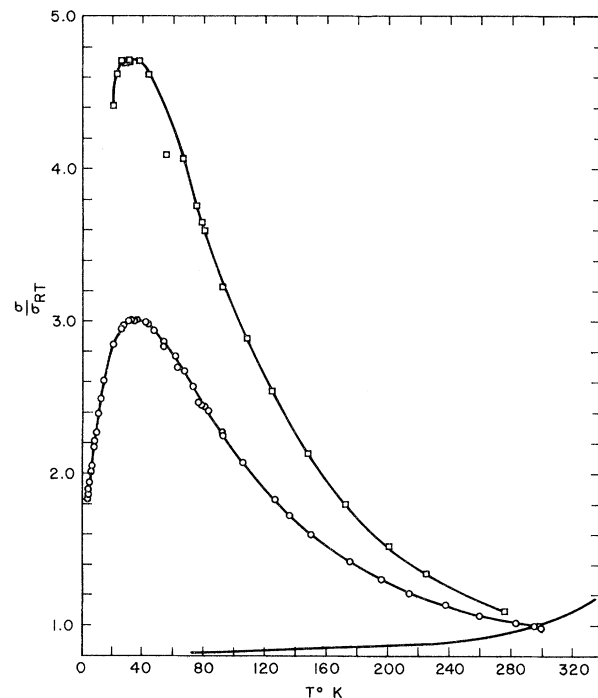


FIG. 1. Temperature dependence of the conductivity of  $(\text{SN})_x$ , normalized to room temperature. Squares, crystal A,  $\sigma_{\text{RT}} = 1730 \Omega^{-1} \text{ cm}^{-1}$ ; circles, crystal B,  $\sigma_{\text{RT}} = 230 \Omega^{-1} \text{ cm}^{-1}$ ; solid line, data on compactions taken from Ref. 13.

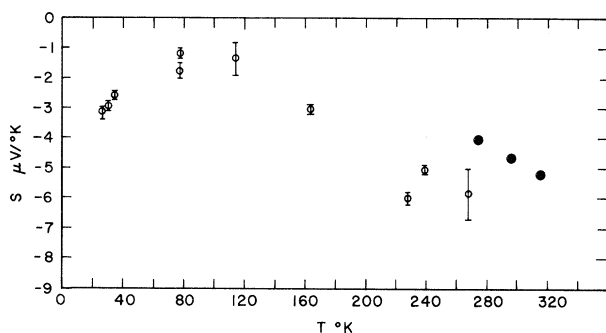


FIG. 2. Seebeck coefficient of  $(\text{SN})_x$  at various temperatures measured with copper-Constantan thermocouples. Data are uncorrected for the thermopower of the Cu leads. Error bars for measurements on crystals; closed circles, values for compactions (at 1750 atm) from Ref. 13.

Six crystals showed room-temperature conductivities of 10, 89, 230, 640, 1470, and 1730  $\Omega^{-1} \text{cm}^{-1}$ , respectively. Earlier data<sup>13</sup> on compactions indicated the average conductivity of  $(\text{SN})_x$  to be between 1 and 25  $\Omega^{-1} \text{cm}^{-1}$  when the chains are randomly oriented. However, compactions of  $(\text{SN})_x$  had indicated the material to have an activated temperature dependence of the conductivity of ca. 0.02 eV. Crystals of  $(\text{SN})_x$  behave like a metal; the temperature dependence of the electrical conductivity is plotted for two crystals (both cooling and heating) in Fig. 1 and compared to compaction data. For both crystals the conductivity passes through a small maximum at 33°K; the value of this maximum varies from 3 to 4.7 times the room-temperature conductivity, indicative of a large number of impurities or defects contributing to the electron scattering. At temperatures below the conductivity maximum, the conductivity falls off only very slightly tending to a constant value.

The large conductivity at 4.36°K suggests that  $(\text{SN})_x$  is metallic despite the conductivity maximum. Seebeck coefficient data (Fig. 2) indicate no critical behavior at the conductivity maximum; a small negative value is observed throughout the entire temperature range studied. Figure 3 is a plot of  $\ln \sigma$  versus  $1/T$  for one crystal, showing that the low-temperature conductivity tends to a constant value at  $T \rightarrow 0^\circ\text{K}$  as expected for impurity scattering. At high temperature a plot of  $\rho$  versus  $T$  (Fig. 4) is linear (although with different slopes for different crystals), indicative of metallic behavior dominated by acoustic-phonon scattering.

Phenomenologically the maximum at 33°K is

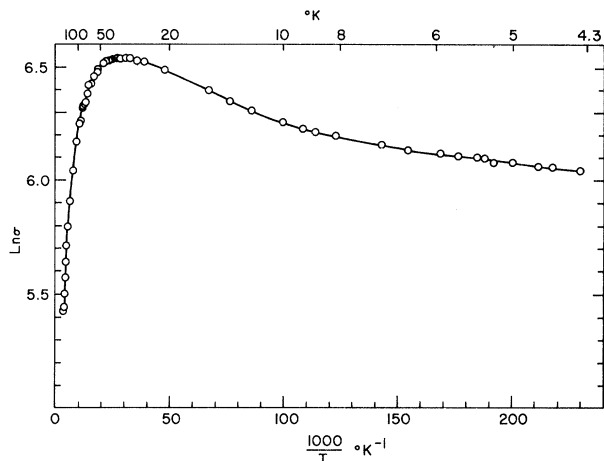


FIG. 3. Natural logarithm of the absolute conductivity of  $(\text{SN})_x$  versus reciprocal temperature (crystal B of Fig. 1). The apparent activation energy just below the conductivity maximum is  $\sim 4 \times 10^{-4}$  eV, corresponding to 4.7°K.

similar to what is observed in metal systems containing small amounts of magnetic impurities, an example being zinc with 300 ppm manganese. This behavior, known as the Kondo effect, arises from the scattering of mobile electrons by impurities or defects with localized magnetic mo-

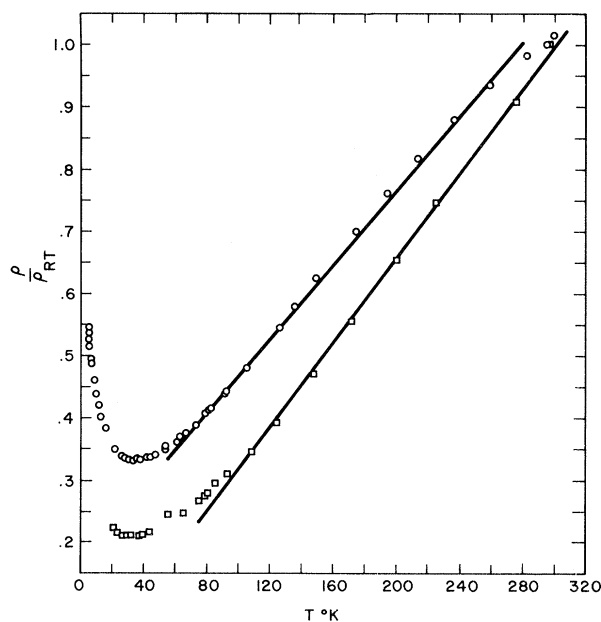


FIG. 4. Temperature dependence of the resistivity of  $(\text{SN})_x$  normalized to room temperature demonstrating linear high-temperature behavior. Squares, crystal A,  $\rho_{\text{RT}} = 5.8 \times 10^{-4} \Omega \text{cm}$ ; circles, crystal B,  $\rho_{\text{RT}} = 4.3 \times 10^{-3} \Omega \text{cm}$ .

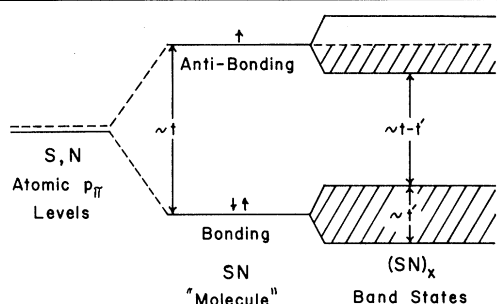


FIG. 5. Molecular-orbital energy-level band scheme for  $(\text{SN})_x$  which predicts metallic behavior. SN anti-bonding molecular orbital contains one unpaired spin per "molecule," which forms a half-filled band in  $(\text{SN})_x$ .

ments.<sup>17</sup> Although  $\rho$  versus  $\ln T$  is linear below the maxima in  $\sigma$  for  $(\text{SN})_x$  as the theory predicts, there is no large increase in the Seebeck coefficient as theory also predicts.<sup>18</sup>

Modifying the arguments of Ref. 14, a simple molecular orbital model of the one-electron band structure predicting the metallic behavior of  $(\text{SN})_x$  is possible and is shown in Fig. 5. The electron transport properties are determined by the transfer integrals between the  $\pi$  orbitals on S and N. There will be two transfer integrals, one associated with the short 1.55-Å bond length denoted by  $t$ , the other associated with the longer bond (1.73 Å) denoted by  $t'$  with  $t' \ll t$ .  $t$  produces the bonding and antibonding orbitals associated with the SN "molecule." These orbitals hold three electrons (two from S and one from N) with one unpaired spin in the antibonding orbital. Introduction of  $t'$  spreads the bonding orbital and antibonding orbital into bands forming one filled band and one half-filled band. The metallic properties are then associated with the half-filled band which at this level of approximation consists of wave functions containing sulfur  $3p_\pi$  orbitals as the main band contributions. The above arguments assume that the sulfur and nitrogen  $\pi$ -electron Coulomb integrals are identical. That the bands do not split from a Peierls instability may be due to the presence of weak interactions between chains.<sup>11a</sup> The S-S distance between chains in the same plane is 3.25 Å, smaller than the normal Van der Waals spacing of  $\sim 3.7$  Å.

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