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Structure and Electronic Properties of Polymeric Sulfur Nitride (SN)_x Modified by Bromine*

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(Received 11 April 1977)

We report the structure and electronic properties of (SNBr_{0.4})_x and the first chemical modification of the polymeric superconductor (SN)_x. Its dc conductivity at 300 K is ten times greater than that for (SN)_x and the thermoelectric power is positive rather than negative. The plasma energy and the superconductivity transition temperature are essentially unchanged. These results suggest that a small displacement of the Fermi level and a large increase in scattering time occur upon bromination.

Since the discovery of the superconducting properties¹ of polymeric sulfur nitride (SN)_x there has been considerable interest in its physical properties and numerous attempts to produce analogous compounds.² We have recently succeeded in modifying the properties of (SN)_x films and crystals by reaction with Br₂, I₂, and ICl.³ Independently, Bernard *et al.*⁴ reported on the addition of bromine to (SN)_x. In this Letter, we make the first detailed report of the structure and electronic properties of crystalline (SN)_x reacted with bromine. We find substantial changes in the dc conductivity $\sigma_{dc}(T)$ and the thermoelectric power $S(T)$ while the plasma energy and the superconducting T_c are essentially unchanged. These striking electronic properties are shown to be consistent with an unusual model for bromine incorporation in (SN)_x as suggested by detailed transmission electron microscopy (TEM) results.

On exposure to the vapor pressure of bromine at room temperature, (SN)_x crystals change from gold to blue-black fibrous crystals of composition (SNBr_{0.5})_x. Evacuation at 10⁻⁵ Torr at room temperature for 1 h results in a final composition (SNBr_{0.4})_x. At this composition, the crystal has expanded ~50% in volume with no measurable expansion in the *b* direction. During the bromination, some exfoliation and macroscopic cracking is observed. The density increases from 2.32 g/cm³ to 2.65 g/cm³.

X-ray precession photographs of individual crystals of (SNBr_{0.4})_x show only (0*k* 0) reflections.³ X-ray powder diffraction results show the ($\bar{1}$ 02) reflection of (SN)_x to be broadened, but unshifted, indicating that the *a* and *c* lattice constants remain unchanged. TEM diffraction re-

sults for (SN)_x and (SNBr_{0.4})_x are shown in Fig. 1. The three most notable features of these data are (1) Bragg diffraction spots appear in approximately the same positions in (SN)_x and (SNBr_{0.4})_x; (2) the (SNBr_{0.4})_x pattern shows considerably more streaking perpendicular to *b**; and (3) diffuse lines are observed perpendicular to *b** at (0 $\frac{1}{2}$ *k* 0). Forbidden reflections observed in both patterns are due to multiple diffraction effects. The unchanged Bragg diffraction spots show that the (SN)_x lattice remains unchanged on bromination in agreement with the powder x-ray data. The increased streaking in the diffraction pattern

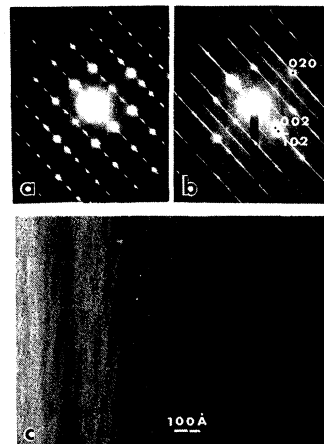


FIG. 1. Electron diffraction pattern from (a) (SN)_x fibers showing the *b***c** reciprocal lattice net; (b) (SNBr_{0.4})_x fibers oriented similarly to (a). The simultaneous occurrence of (002) and ($\bar{1}$ 02) reflections and the larger streaks are attributed to extensive twinning; and (c) electron micrograph of (SNBr_{0.4})_x twinned fibers with 20-Å dimensions.

is consistent with increased disorder of the fibers. The observation of superlattice lines in Fig. 1(b) at the $(0\frac{1}{2}k0)$ interval suggests either doubling of the $(\text{SN})_x$ lattice along b or superposition of a commensurate bromine lattice ordered only along the chain axis with a period of $2b$. Doubling of the $(\text{SN})_x$ lattice along b seems unlikely since all the Bragg diffraction spots of Fig. 1(b) can be accurately indexed as arising from the $(\text{SN})_x$ lattice with the lattice parameters unchanged. With this structural data the most plausible model of $(\text{SNBr}_{0.4})_x$ is one in which the Br_2 does not enter the $(\text{SN})_x$ lattice but instead resides in the interfiber regions. High-resolution electron microscopy indicates a fiber diameter of 50–70 Å for $(\text{SN})_x$ and 20–30 Å for $(\text{SNBr}_{0.4})_x$. Figure 1(c) is a dark field micrograph of $(\text{SNBr}_{0.4})_x$ showing fine structure parallel to the $(\text{SN})_x$ chain direction. These fine striations, thought to be $(\text{SN})_x$ microtwins, are observed with 20-Å intervals in some areas. Chemical elemental analysis in the TEM established that the samples are compositionally homogeneous on a scale of 1–2 μm .

The electrical conductivity of $(\text{SNBr}_{0.4})_x$ was measured both parallel and perpendicular to the b axis. At 300 K conductivity as high as $\sigma_{\parallel} = 2 \times 10^4 \Omega^{-1} \text{cm}^{-1}$ was measured while σ_{\perp} , measured on only a few samples, ranged between 15 and 40

$\Omega^{-1} \text{cm}^{-1}$. The temperature dependence of the resistivity and thermopower S are shown in Fig. 2. Comparison with $(\text{SN})_x$ ^{5,6} shows that σ_{RT} increases about an order of magnitude while S changes from negative to positive values. The parallel resistivity ρ_{\parallel} decreases monotonically, becoming constant below 3 K until the onset of superconductivity at $T_c \approx 0.3$ K. The temperature dependence of the transverse resistivity ρ_{\perp} differs qualitatively from that observed⁵ in $(\text{SN})_x$ by decreasing monotonically to 3 K, below which it also becomes constant. The magnitude of S is small and decreases approximately linearly with temperature with a possible phonon drag peak appearing near 60 K. T_c for a number of crystals varied between 0.25–0.32 K, which is the same range over which T_c varies for $(\text{SN})_x$ crystals. In some $(\text{SNBr}_{0.4})_x$ crystals the transition width was considerably narrower ($\Delta T_c = 10$ –20 mK) than we have ever observed in $(\text{SN})_x$ ($\Delta T_c = 50$ –60 mK) and the onset of superconductivity was always comparatively sharp.

The polarized reflectance of a crystalline $(\text{SN})_x$ sample before and after bromination is shown in Fig. 3. Unexpectedly, despite the increase of σ_{dc} upon bromination, the plasma edge has been red-shifted out of the visible region. A Drude-Loorentz analysis of the $E \parallel b$ brominated spectrum yields a plasma energy $\hbar\omega_p = 5.0 \pm 1$ eV, a scatter-

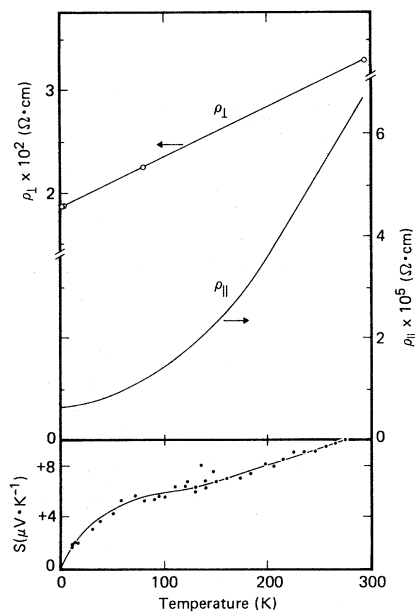


FIG. 2. Temperature dependence of the dc resistivities $\rho_{\parallel b}$ and $\rho_{\perp b}$ and the absolute thermoelectric power $S \parallel b$ for crystalline $(\text{SNBr}_{0.4})_x$. Data for ρ_{\perp} were only obtained at points shown.

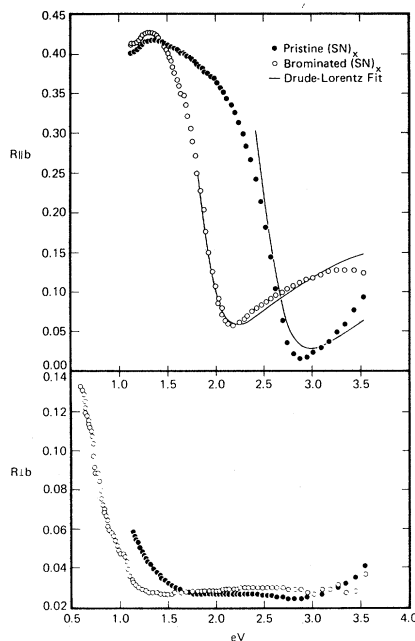


FIG. 3. Polarized reflectance of the same $(\text{SN})_x$ crystal before and after bromination. The fit to $R \parallel b$ before bromination is taken from Fig. 2 in Ref. 7.

ing lifetime $\tau_{\text{opt}}/\hbar = 1.8 \pm 0.3 \text{ eV}^{-1}$, and a real part of the dielectric constant at the reflectance minimum $\epsilon_1^B(E_{\text{min}}) = 6.48$. These values are to be compared with $\hbar\omega_p = 4.6 \pm 1 \text{ eV}$, $\tau_{\text{opt}}/\hbar = 1.6 \pm 0.3 \text{ eV}^{-1}$, and $\epsilon_1^B(E_{\text{min}}) = 3.6$ from Grant, Greene, and Streit⁷ for $(\text{SN})_x$. We see that, within experimental error, there is little change in $\hbar\omega_p$ or τ_{opt} upon bromination. Most of the observed spectral shift seems due to an increase in background dielectric constant presumably associated with the included Br_2 molecules.

We turn now to a discussion of possible structural and electronic models of $(\text{SNBr}_{0.4})_x$. The large volume increase of the $(\text{SN})_x$ crystals on reaction with bromine immediately suggests intercalation of bromine between $(\text{SN})_x$ chains. However, the unchanged lattice parameters are not consistent with such a model. Structural data suggests that $(\text{SNBr}_{0.4})_x$ consists of 20–30-Å-diam fibers of $(\text{SN})_x$ with Br_2 located between the fibers. The assumption that the bromine is diatomic is based on observation of the 323-cm^{-1} Raman mode of free Br_2 shifted to 230 cm^{-1} in $(\text{SNBr}_{0.4})_x$.⁸ Within this picture of the structural features we need to reconcile the large increase in σ_{dc} and the change in sign of S with the essentially unchanged σ_{opt} and T_c . We believe that the main effect of bromination is to increase the dc scattering lifetime τ_{dc} and that charge-transfer effects are relatively weak. Based on the simple relation $\sigma_{\text{opt}} = \omega_p^2 \tau_{\text{opt}} / 4\pi$, the results suggests that different mechanisms for τ_{opt} and τ_{dc} are operative in brominated $(\text{SN})_x$ as they probably are in pristine $(\text{SN})_x$. The latter assertion is reinforced by the observation that σ_{opt} is temperature and pressure insensitive⁹ while σ_{dc} has a strong temperature and pressure dependence.¹⁰

Although there may only be small shifts of E_F in brominated $(\text{SN})_x$ and hence small changes in density of states and plasma energy, significant changes in the shape of portions of the Fermi surface are not out of the question since E_F crosses several weakly dispersive bands.¹¹ Fermi-surface averages govern both electron-phonon and electron-electron scattering and could be the source of large changes in τ_{dc} with bromination, especially for the latter where severe selection-rule changes might occur for the hole-electron interpocket scattering.¹² Those surfaces of the Fermi surface perpendicular to interpocket directions in the Brillouin zone could be affected by any interchain effects imposed by bromination. The relative contribution of holes and electrons to S could also change with changing Fermi sur-

face.

Considering the major changes in properties of $(\text{SN})_x$ caused by reaction with bromine, the negligible change in T_c was surprising. The most plausible reasons for unchanged T_c are either that large cross-section fibers of $(\text{SN})_x$ remain unpenetrated by bromine and hence short out the sample at T_c of $(\text{SN})_x$, or that the electron-phonon coupling constant $\lambda = N(E_F)\langle I^2 \rangle / M\langle \omega^2 \rangle$ remains practically undisturbed for $(\text{SNBr}_{0.4})_x$. The first possibility implies that the T_c of $(\text{SNBr}_{0.4})_x$ is depressed below the T_c of $(\text{SN})_x$. The second possibility would allow us to estimate the maximum shift in E_F , and hence charge transfer, that is consistent with no detectable change in T_c , under the assumption that the change in λ is only due to $N(E_F)$. From the theoretical conduction-band density of states for $(\text{SN})_x$ ¹¹ we obtain a maximum of 0.12 holes per Br atom.¹³ The apparent constancy of λ in the presence of large changes in σ_{dc} would provide further support for the suggestion that τ_{dc} is dominated by electron-electron scattering¹² rather than electron-phonon scattering.

We have presented some physical properties of the first significant chemical modification of $(\text{SN})_x$, i.e., $(\text{SNBr}_{0.4})_x$. It seems clear from this work that many new modifications of $(\text{SN})_x$ will now be found. We have already reacted I_2 and ICl with $(\text{SN})_x$ and the properties of all these compounds which can be prepared with a range of halogen content are under investigation. Much needs to be done to determine fully the details of the bromine interaction with $(\text{SN})_x$. The origin of the commensurate superlattice structure along the b axis is not yet clear and possible effects of this ordering on the electronic properties remain to be answered by future work.

The support and critical comments of B. H. Schechtman are gratefully acknowledged. The technical assistance of R. L. Bingham and J. E. Vazquez has been invaluable in this work.

*Work supported in part by the Office of Naval Research under Contract No. N00014-76-C-0658.

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⁸Compare with Raman mode at 240 cm^{-1} for Br_2 intercalated graphite reported by J. J. Song, D. D. L. Chung, P. C. Eklund, and M. S. Dresselhaus, *Solid State Commun.* 20, 1111 (1976).

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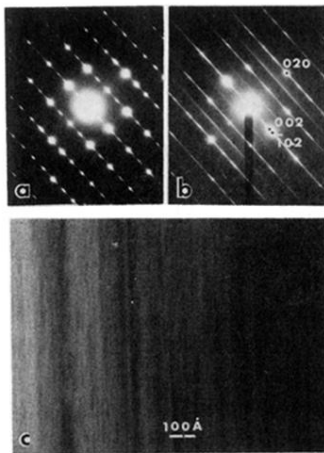


FIG. 1. Electron diffraction pattern from (a) $(\text{SN})_x$ fibers showing the b^*c^* reciprocal lattice net; (b) $(\text{SNBr}_{0.4})_x$ fibers oriented similarly to (a). The simultaneous occurrence of (002) and $(\bar{1}02)$ reflections and the larger streaks are attributed to extensive twinning; and (c) electron micrograph of $(\text{SNBr}_{0.4})_x$ twinned fibers with 20-Å dimensions.