Modification of the Electronic Properties of $(SN)_x$ by Halogens; Properties of $(SNBr_{0\cdot4})_x$

By G. BRYAN STREET,* W. D. GILL, R. H. GEISS, R. L. GREENE, and J. J. MAYERLE
(*I.B.M. Research Laboratory, 5600 Cottle Road, San Jose, California* 95193)

Summary The electrical and optical properties of $(SN)_x$ have been modified by reaction with Br_2, ICl, and I_2.

SINCE the discovery of the superconducting properties of polymeric $(SN)_x$ there has been great interest in producing analogous compounds.[1] We have obtained several new materials by the reaction of $(SN)_x$ films and crystals with Br_2, I_2, or ICl. The electrical conductivity of the brominated $(SN)_x$ (the most extensively studied to date) was permanently increased by an order of magnitude at room temperature for both films and crystals, and the colour changed to blue-black instead of the gold of normal $(SN)_x$. During this investigation Bernard *et al.*[2] reported their results on the addition of bromine to $(SN)_x$; however, their structural results and interpretation are different from ours and they report no electrical measurements. Bromine can be incorporated from the vapour phase or from solution in amounts dependent upon its vapour pressure or concentration. Exposure of $(SN)_x$ crystals to the vapour pressure of dry bromine at room temperature for about 24 h yields blue-black fibrous crystals of composition $(SNBr_{0\cdot5})_x$. Evacuation at 10^{-5} Torr for 30 min at ambient temperature results in a final composition $(SNBr_{0\cdot4})_x$. This composition results in an expansion of *ca.* 50% in volume of the original crystal in directions perpendicular to the $(SN)_x$ chain axis. Owing to an increase in the rotational disorder of the fibres after bromination, *X*-ray precession photographs of individual crystals of $(SNBr_{0\cdot4})_x$ show only $0k0$ reflections. However, *X*-ray powder and single-crystal electron diffraction data show that despite the *ca.* 50% volume expansion, the *a* and *c* lattice constants remain essentially unchanged from those of pristine $(SN)_x$. The electron diffraction studies on $(SNBr_{0\cdot4})_x$ also show that the *b* lattice parameter is double that of $(SN)_x$. This result is consistent either with a doubling of the $(SN)_x$ lattice along *b* or with a superposition of a commensurate bromine lattice ordered only along the chain axis with a period of 2*b*. Since *a* and *c* do not change, we believe that the chain geometry does not change significantly and the bromine does not enter the $(SN)_x$ lattice but instead resides in the interfibre regions. Very high resolution electron microscopy indicates a fibre diameter of 50—70 Å for $(SN)_x$ and *ca.* 30 Å for $(SNBr_{0\cdot4})_x$. The measured density, 2·65 g cm^{-3}, of a sample of $(SNBr_{0\cdot4})_x$ compositionally homogeneous on a 2—3 μm scale, is also consistent with the presence of bromine between these *ca.* 30 Å diameter fibres of $(SN)_x$, as is a Raman band at 230 cm^{-1} which can be assigned to a Br–Br vibration of a weakly bonded Br_2 molecule.[3] Thermal analysis shows that the major portion of the bromine is liberated only on heating to 135—150 °C. Since at these temperatures $(SN)_x$ itself is volatile this heating results in deposition of highly conducting brominated $(SN)_x$ films. The conductivity of $(SNBr_{0\cdot4})_x$ crystals is approximately an order of magnitude higher than that of $(SN)_x$ with values of σ = *ca.* 2×10^4 Ω^{-1} cm^{-1} at 298 K. The conductivity increases by approximately an order of magnitude on cooling to 4 K and σ at 298 K increases with hydrostatic pressure, verifying the electronic nature of the conductivity. The $(SNBr_{0\cdot4})_x$ crystals superconduct with T_c *ca.* 0·31 K. This transition temperature is similar to that of $(SN)_x$ crystals and provides further evidence that the $(SN)_x$ chain structure within the *ca.* 30 Å diameter fibres remains unchanged after bromination.

We thank D. Miller and R. Bingham for technical assistance and the Office of Naval Research for partial support.

(*Received, 4th March* 1977; *Com.* 194)

[1] G. B. Street and R. L. Greene, *I.B.M. J. Res. Develop.*, 1977, **21**, 99.
[2] C. Bernard, A. Herold, M. Lelaurain, and G. Robert, *Compt. rend. (C)*, 1976, **283**, 625.
[3] P. Klaboe, *J. Amer. Chem. Soc.*, 1967, **89**, 3667.