

PROPERTIES OF BROMINATED $(SN)_x$

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The structure and electronic properties of brominated $(SN)_x$ are briefly reviewed. The large increase in conductivity σ on bromination together with the small change in T_c and the small pressure dependence of σ suggest that electron-hole scattering processes, which dominate the conductivity of $(SN)_x$, are suppressed due to lowering of the Fermi level by charge transfer to the included bromine.

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After many unsuccessful attempts to prepare polymeric modifications of $(\text{SN})_x$, intercalation by halides has (recently) been shown to result in substantial structural and electronic modification of $(\text{SN})_x$.¹⁻³ Bromination results in the largest changes in electronic properties, thus brominated $(\text{SN})_x$ has been most extensively studied.⁴

On bromination $(\text{SN})_x$ crystals change from gold to blue/black and expand ~50% in volume in directions perpendicular to the b-axis. Transmission electron microscopy shows that brominated $(\text{SN})_x$ has an almost unchanged (but more disordered) $(\text{SN})_x$ lattice with a strong commensurate super lattice with period $2b$ suggesting that bromine intercalates between $(\text{SN})_x$ fibres in a 1-D ordered structure. X-ray diffraction measurements have shown that the $(\text{SN})_x$ 'a' and 'c' lattice parameters are changed slightly on bromination, indicating that some bromine is also included within the $(\text{SN})_x$ fibers.⁵ Raman spectroscopy studies^{5,6} have shown that Br_3^- is the major molecular species present in the intercalated material. However IR studies⁷ suggest that the Br_2 species is also present.

Bromination of $(\text{SN})_x$ to a composition $(\text{SNBr}_{0.4})_x$ results in a tenfold increase of b-axis conductivity to $\sigma_{||} = 2 \times 10^4 \Omega^{-1} \text{cm}^{-1}$. The thermopower changes sign from n-type to p-type consistent with electron transfer from $(\text{SN})_x$ to the bromine.² However the plasma frequency obtained from optical reflectivity remains essentially unchanged from $(\text{SN})_x$ indicating that the main effect of bromination is to increase the dc scattering lifetime.² The superconducting T_c of the brominated crystals was also found to remain essentially unchanged² (T_c increases 10 to 20% for $(\text{SNBr}_{0.4})_x$). This

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result indicating only small changes in the density of states at E_F is also consistent with a shift $\leq 1\text{eV}$ of the Fermi level due to charge transfer.

We have recently measured the pressure dependence of both the normal conductivity and the superconductivity in brominated $(\text{SN})_x$.⁸ In contrast to $(\text{SN})_x$ where σ increases by more than 40%/kbar, in $(\text{SNBr}_{0.4})_x$ σ only increases by $\sim 1.3\%$ /kbar. In brominated $(\text{SN})_x$, T_c is observed to decrease monotonically with hydrostatic pressure in sharp contrast to the increase of T_c with pressure seen with $(\text{SN})_x$. Other studies of the superconducting properties of brominated $(\text{SN})_x$ show a more complete and better defined Meissner effect,⁹ a narrower transition width to the superconducting state^{2,10} and a more usual critical field versus T_c behavior¹⁰ than is observed in $(\text{SN})_x$. The conclusion from the superconductivity experiments is that in brominated $(\text{SN})_x$ the fibers are better coupled in the superconducting sense leading to a more nearly 3-D superconductivity behavior than found in $(\text{SN})_x$.¹⁰

How can the normal conductivity properties in brominated $(\text{SN})_x$ be explained? For a semimetal such as $(\text{SN})_x$, charge transfer from bromine does not change the total carrier density. In $(\text{SN})_x$ the resistivity is well described by a T^2 dependence which is believed to be due to dominance of electron-hole scattering processes even at high temperature.¹¹ The strong pressure dependence of σ in $(\text{SN})_x$ would be a consequence of the sensitivity of the electron-hole scattering processes to details of the Fermi surface.¹² In brominated $(\text{SN})_x$ suppression of electron-hole

scattering can be reasonably expected from Fermi surface considerations. Charge transfer to bromine in $(\text{SNBr}_{0.4})_x$ can be assumed to remove approximately 0.1 electrons/SN unit from the conduction band, lowering E_F by about 1eV. Lowering E_F causes an expansion of the hole pocket volume and a contraction or possibly elimination of the electron pockets and results in suppression of electron-hole scattering. As this scattering process is suppressed we expect an increase of the dc scattering lifetime causing an increase in σ . Electron-phonon scattering processes should begin to dominate resulting in a deviation from the T^2 dependence of ρ toward a more linear temperature dependence and the pressure dependence of σ should decrease sharply since scattering is no longer very sensitive to details of the Fermi surface. In fact the observed T-dependence of σ in $(\text{SNBr}_{0.4})_x$ is between linear and quadratic and the pressure dependence is adequately accounted for by lattice stiffening effects usually dominant in metals. Thus this model invoking Fermi surface changes due to charge transfer on bromination and subsequent suppression of electron-hole scattering, explains the major features of the electronic properties of brominated $(\text{SN})_x$.

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