Electrical Resistivity Studies on Hepta-Copper-Tetra-sulphur-Tetra-nitride - $Cu_7S_4N_4$

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$Cu_7S_4N_4$, (a compound prepared by the reaction of copper (plates) and S_4N_4 in CCl_4 solution) exhibits semiconducting property. When either Cu or Ni powders are added to this, the semiconducting property is retained; but addition of a mixture of Cu and Ni powder in the same ratio converted it to a good conductor. The activation energy is greater for the doped samples and varies with temperature.

The versatile chemistry of tetrasulphur tetranitride (S_4N_4) has been built on the stable sulphur-nitrogen bond network which can undergo a variety of reactions with both metals and nonmetals [1]. A very interesting aspect of S_4N_4 chemistry is cleavage of bonds when S_4N_4 vapour is passed over heated silver gauze in vacuum. S_4N_4 in a nonprotonated solvent like CCl_4 at room temperature yielded a blue black flaky solid when treated with copper and silver metals (powder and foils) which analysed to the chemical formula of $Cu_7S_4N_4$ and $Ag_5S_4N_4$ [3]. The solid copper compound was found to be paramagnetic and the IR studies showed the absence of S_4N_4 in the molecule, but presence of weak S-N bonds. This indicated opening of S_4N_4 ring and copper reactively inserting itself into the layers of S-N chains thereby incorporating seven copper atoms. An XRD showed the solid $Cu_7S_4N_4$ to be amorphous; but crystallization occured when $Cu_7S_4N_4$ was maintained at 110° C for 4-5 days. The crystal strucutre was found to be orthorhombic with lattice parameters of a = 3.93 Å, b = 3.88 Å and c = 5.45 Å.

The amorphous material was pelletized and the resistivities measured from room temperature down to liquid nitrogen and liquid helium temperatures. The samples indicated a nearly semiconduting behaviour. Elemental copper and nickel have a tendency to react with S. So it was interesting to study the effect of

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addition of small amounts of elemental copper and nickel powders to $Cu_7S_4N_4$ to see if this would alter electron overlap and conductivity. The results of such study are discussed here.

SAMPLES AND MEASUREMENTS

$Cu_7S_4N_4$ was mechanically mixed thoroughly with Cu and Ni powders in specified weight ratios. The resulting mixtures were pelletised at a pressure of 180 Kp/cm^{-2} into pellets of diameter 0.8 cm by 0.1 cm thickness. The electrical contacts were attached to the surface of the pellets with the help of conducting silver paste. The resistance of each pellet was measured using a standard four probe technique from room temperature down to liquid nitrogen and liquid helium temperature in steps of 5° C.

Keithley 220 programmable current source was used for passing the current and Keithley 195A digital multimeter was used for measuring the voltage across the probes. The temperature was measured using temperature controller Model DRC 80° C of Lakeshore Cryotionic Inc.

RESULTS AND DISCUSSIONS

Pellets of the following samples were prepared:

(a) $Cu_7S_4N_4$
(b) $Cu_7S_4N_4$ + Cu (in weight ratio 5:1) (mol. ratio 3:5)
(c) $Cu_7S_4N_4$ + Ni (in weight ratio 5:1) (mol. ratio 3:5)
(d) $Cu_7S_4N_4$ + Cu+Cu (in weight ratio 5:1:1) (mol. ratio 3:5:5)
(e) $Cu_7S_4N_4$ + Ni+Ni (in weight ratio 5:1:1) (mol. ratio 3:5:5)
(f) $Cu_7S_4N_4$ + Cu+Ni (in weight ratio 5:1:1) (mol. ratio 3:5:5)

The i-V characteristics of all pellets showed ohmic behaviour. So resistance was measured by measuring voltage drop with a known current.

The resistance of these pellets were measured as a function of temperature and the results (plots of log R/R_{300} *vs* 1/T) are presented in figs 1-6 and are summerised in Table 1.

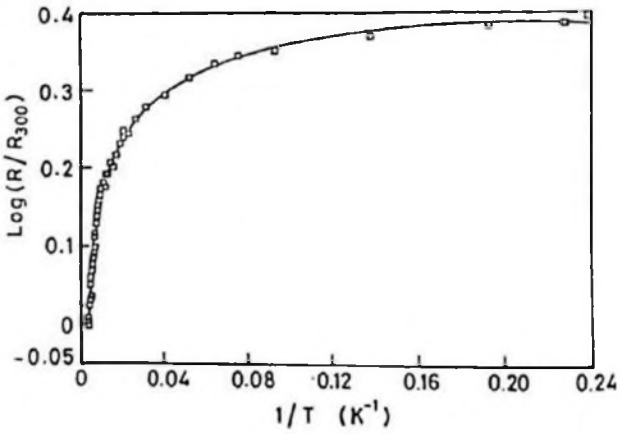


Fig 1 **Log (R/R_{300}) vs 1/T plots;** Sample $Cu_7S_4N_4$

The results in Table 1 clearly shows that addition of small quantity of Cu has increased resistivity at room temperature to 200 ohm cm and addition of Ni increased it to 27 ohm cm indicating that the reaction of Cu with S has reduced the electron overlap and localised the charges.

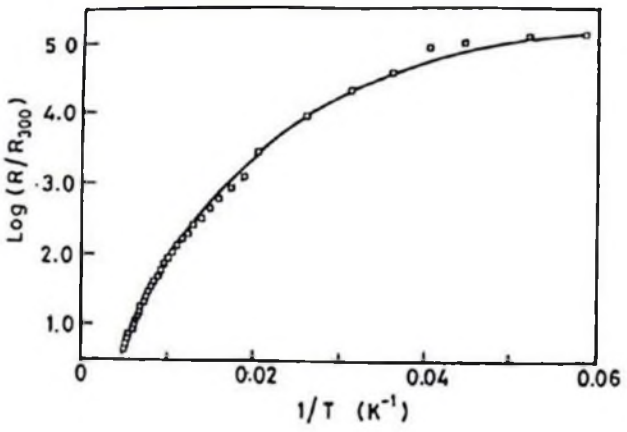


Fig 2 Log (R/R_{300}) vs 1/T plots; Sample $Cu_7S_4N_4$ + Cu

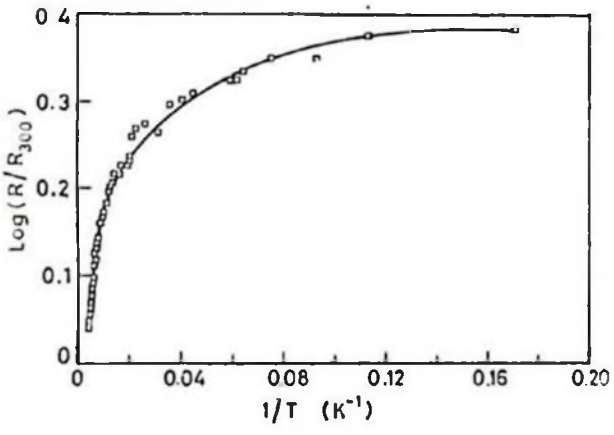


Fig 3 Log (R/R_{300}) vs 1/T plots; Sample $Cu_7S_4N_4$ + Ni

Samples a to e showed semicondcting behaviour. The R-T graphs indicated the activation energy to be temperature dependent. The activation energy values were calculated at different temperature ranges from the slopes and included in Table 1.

Table 1

Measured properties of Different Pellets

Pellet Sample	Resistivity at Room Temp	< - - Activation Energy - - > Temp range (K)	Energy (eV)
a	0.005 ohm cm	50 - 240	0.0191
		5 - 20	0.0001
a	200 ohm cm	50 - 240	0.0560
		5 - 20	0.0240
c	27 ohm cm	50 - 240	0.0097
		20 - 50	0.0071
		5 - 20	0.0050
d		145 - 300	0.080
		77 - 145	0.049
e		130 - 300	0.040
		77 - 120	0.005
f		Metallic in behaviour	

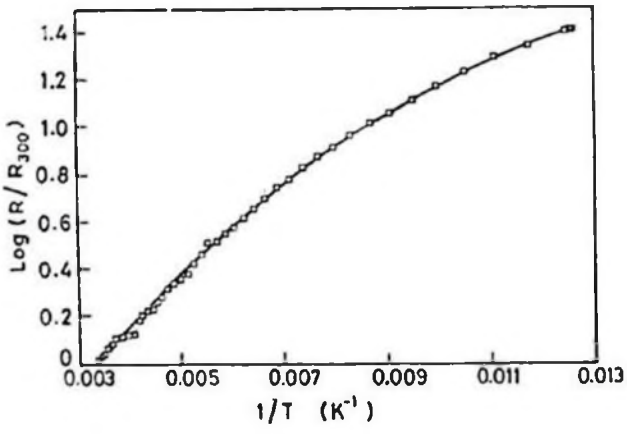


Fig 4 Log (R/R_{300}) vs 1/T plots; Sample $Cu_7S_4N_4$ + Cu + Cu

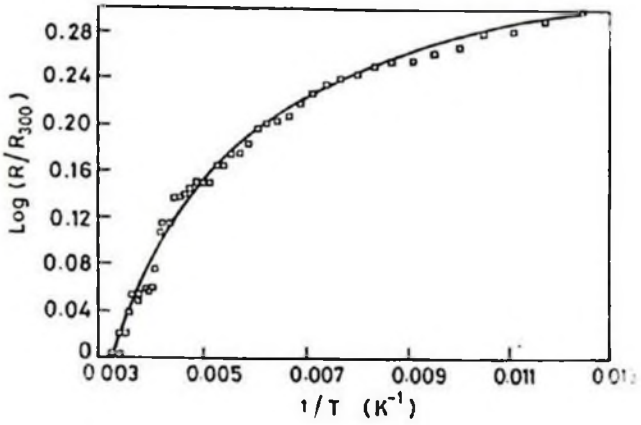


Fig 5 Log (R/R_{300}) *vs* 1/T plots; Sample $Cu_7S_4N_4$ + Ni + Ni

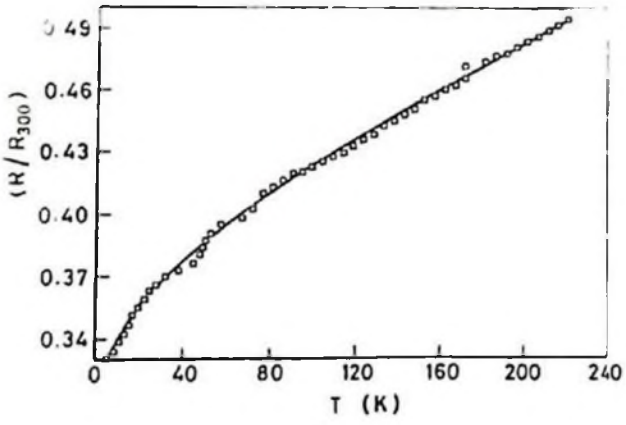


Fig 6 (R/R_{300}) *vs* 1/T plots; Sample $Cu_7S_4N_4$ + Cu + Ni

Sample f, $Cu_7S_4N_4$ + Ni + Cu mixture (5:1:1) has a high resistivity of 1100 ohm cm at room temperature. But the linear R/R_{300} *vs* T graph (fig. 6) shows the material to be exhibiting metallic behaviour.

This is interesting that addition of a single metal does not alter the semiconducting property. Even when additional Cu powder is added to $Cu_7S_4N_4$ + Cu (in sample d) or Ni powder to $Cu_7S_4N_4$ + Ni (in sample e), the material retains semiconducting property. However, addition of a mixture of Cu and Ni to $Cu_7S_4N_4$ in the same weight ratio (in sample f) changes the property to metallic conduction indicating good overlap of electron orbitals in the admixture material.

The above experimental results indicate that the addition of copper or nickel powder to $Cu_7S_4N_4$ enhances the chemical reactivity with sulphur, reduces the electron overlap leading to reduced conductivity. The R-T graphs indicate that the activation energy is temperature dependent and a variable range hopping model is applicable for the interpretation of the results. However, in the presence of copper and nickel, metallic behaviour is observed indicating decrease in energy gap or activation energy.

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