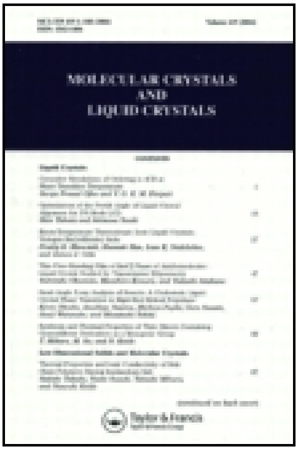

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Electrical Properties of 3, 4, 5-Tris (Alkylthio) -1, 2-Dithiolium Charge Transfer COMPLEXES

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ELECTRICAL PROPERTIES OF 3,4,5-TRIS(ALKYLTHIO) -1,2-DITHIOLIUM CHARGE TRANSFER COMPLEXES

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The dc-conductivity of the charge transfer complexes of 3,4,5-tris (alkylthio)-1,2-dithiolium with tetracyanoquinodimethane, $M(dmit)_2$ (where M=Ni, Pt, Pd and dmit=dimercaptoisotrithione), etc. for a wide range of temperature is reported.

4,5-Bis(alkylthio)-1,2-dithiole-3-thiones react with methyl iodide to give 3,4,5-tris(alkylthio) -1,2- dithiolium iodides [1] . These compounds give a number of charge transfer (CT) complexes with tetracyanoquinodimethane (TCNQ), with $M(dmit)_2$ (where M=Ni,Pt,Pd and dmit=dimercaptoisotrithione), etc. [1], [2]. Preliminary results of the conductivity measurements at room temperature in polycrystalline compressed discs of these complexes have been reported in [1] and [2]. In this paper the electrical properties of the above CT complexes are described in detail. In a few cases the dc-conductivity of single crystals over a wide range of temperature was measured and compared with that of other similar conducting solids.

At room temperature the dc-conductivity (σ_{RT}) of single crystals, measured along the needle-axis (Z) by a four-probe technique, was $1\Omega^{-1}cm^{-1}$ (average of six samples) for [3,4,5-tris (methylthio)-1, 2-dithiolium $]_{0.5}$ (TCNQ), $4\Omega^{-1}cm^{-1}$ (average of four samples) for [4,5-(propylenedithio)-3-(methylthio) 1,2-dithiolium$]_{0.5}$(TCNQ), 5,1 and $0.7\Omega^{-1}cm^{-1}$ for [3,4,5-tris(methylthio)-1, 2-dithiolium$]_{0.5}$M(dmit)$_2$, where M = Ni, Pt and Pd, respectively. The dc-conductivity of Z_x [Ni(dmit)$_2$] where (Z=n-Bu$_4$Ni, x<1), see ref. [3-5], at room temperature was found to be of the same order of magnitude. Fig. 1 shows the variation of conductivity (σ) with temperature and inverse temperature for a single crystal of [4,5-(propylenedithio)-3-(methylthio)-1,2-dithiolium $]_{0.5}$ (TCNQ) along the needle-axis direction (Z). Fig.2 shows the variation of conductivity with temperature and inverse temperature for a compressed disc of [3,4,5-tris(methylthio)-1,2-dithiolium $]_{0.5}$ Ni(dmit)$_2$ ($\sigma_{RT}=3\Omega^{-1}cm^{-1}$). Although semiconductors at room temperature, the materials show some indication that they may undergo semiconductor/metal phase changes above the room temperature. The activation energy for a single crystal of [4,5-(propylenedithio)-3-(methylthio)-1,2-dithiolium $]_{0.5}$(TCNQ) in the region of 25-50K was found to be 25meV(average of two samples). The activation energy for a polycrystalline disc of [3,4,5-tris (methylthio)-1,2-dithiolium $]_{0.5}$Ni(dmit)$_2$was found to be 30meV between 25 and 60K. The activation energy for a single crystal of $(Bu_4N)_{0.25}$ $Ni(dmit)_2$ (prepared by the method E, ref. [3], from a "trinclinic" crystal of Bu_4N $Ni(dmit)_2$ [4]) was found to be of the same order of magnitude [4].

From the stoichiometry of the compounds it appears that the conduction process will involve the TCNQ or $M(dmit)_2$ molecules rather than the sul-

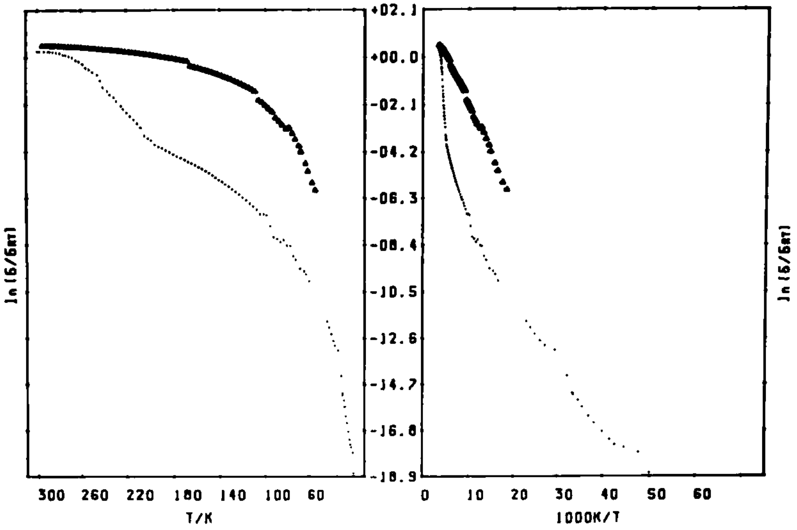

Fig.1. Variation of conductivity with temperature and inverse temperature for a single crystal of [4,5-(propylenedithio)-3-(methylthio)-1,2-dithiolium]$_{0.5}$ (TCNQ). It exhibits sharp drops in conductivity with decreasing temperature (▲▲▲).The conductivity shown originaly at room temperature was recovered on warming (●●●●). The breaks are probably due to the microcracks forming in the crystal.

fur containing (or Bu_4N) cations. The so-called complex TCNQ salts of stoichiometry M^{+}(TCNQ) (where M^+ is a monovalent cation) can be grouped into three large classes, each characterized by their similarity in physical properties [6]. The high conductivity class compounds exhibit conductivities of 10-100Ω^{-1}cm^{-1} at room temperature, metallic behaviour at room temperature, a metal semiconductor transition at lower temperature and a low

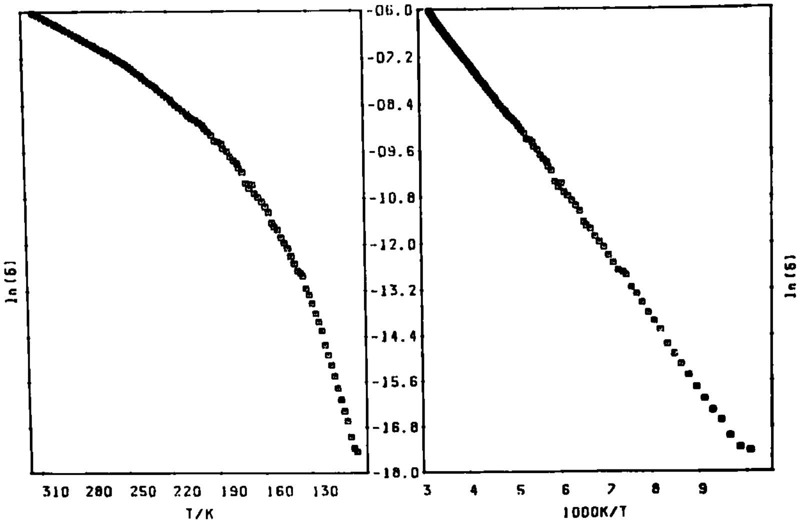

Fig.2. Variation of conductivity with temperature and inverse temperature for a polycrystalline disc of $[\text{3,4,5-tris(methylthio)-1,2-dithiolium}]_{0.5}\ \text{Ni(dmit)}_2$.

activation energy (20-30meV) below the transition. The complexes of the intermediate class exhibit conductivities smaller by several orders of magnitude and semiconducting behaviour at room temperature with an activation energy of 200-300meV .

The third class are practically insulators at room temperature.

The compounds of this investigation do not clearly fall into either the high-or the intermediate-conductivity class of compounds. The most consistent picture is that of a high conductivity class compounds with an unusually high metal/insulator transition above room temperature. This would be consistent with the rather low room temperature conductivity, the small activation energy in the semiconductor region, and the slowly increasing conductivity with temperature at room temperature.

The conductivity of the polycrystalline compressed discs of these compounds do not differ considerably than that of single crystals in the needle axis direction. Also the polarised reflectance spectra do not show large differences if the polarization of the light is changed. Fig.3 shows,

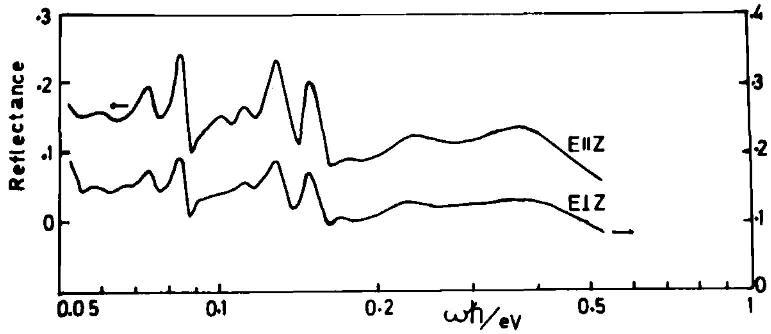

Fig.3. Polarized reflectance spectra of a single crystal of [3,4,5-tris(methylthio)-1,2-dithiolium]$_{0.5}$ (TCNQ).

for example, the polarized reflectance spectra of a single crystal of [3,4,5-tris(methylthio)-1,2-dithiolium]$_{0.5}$(TCNQ) observed at room temperature with the wave-vector(E) parallel (E$\parallel$Z) and perpendicular (E$\perp$Z) to the needle axis (Z).The last observations and the unusually high transition temperature indicate that the compounds are two- or three-dimensional semiconductors.These results must await detailed structural studies which will show the extent of interaction of the sulfur in the cation with the TCNQ or Ni(dmit)$_2$ stacks.

References

[1] G.C.Papavassiliou, Chem.Scripta 25,167 (1985).

[2] G.C.Papavassiliou, E.I.Kamitsos, and J.S. Zambounis,Mol.Cryst.Liq.Cryst. 120,315 (1985); G.C.Papavassiliou, J.S.Zambounis and S.Y. Yiannopoulos,unpublished work.

[3] G.C.Papavassiliou, Z.Naturforsch. 37b, 825 (1982).

[4] G.C.Papavassiliou, J.Physique C3 44, 1257 (1983);G.C.Papavassiliou et al,to be published.

[5] L.Valade,J.-P.Legros,M.Bousseau,P.Cassoux, M.Garbauskas and L.V.Interrante,J.Chem.Soc. Dalton 783 (1985).

[6] J.F.Shchegolev,Phys.Stat.Sol.(a) 12, 9 (1972).