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ANISOTROPY OF THERMOPOWER AND CONDUCTIVITY IN TCNQ COMPLEX SALTS

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ABSTRACT

The observed anisotropy reflects a 2D array of TCNQ's. A plateau in the logσ vs T^{-1} plots is computer fitted to the Roberts-Schmidlin model of states in the band-gap, with electrons as majority carriers. The predicted Seebeck coefficient is correct in sign (negative) and temperature-dependence, but too large, suggesting a hole contribution to the carriers; structural disorder is clearly a factor.

INTRODUCTION

The monoclinic diethyl bipyridilium complex $(DEBP)^{2+}(TCNQ)_4^{2-}$ shows conductivities in the plane of the TCNQ sheet, $\sigma_b \tilde{>} \sigma_c$ and 20-30 times σ_a across the planes of the cations. The triclinic triethylammonium complex $TEA^+(TCNQ)_2^-$ shows a 2000 greater conductivity (RT) along the stacking axis of the TCNQ's (here the a axis), and a much more marked anisotropy, $\sigma_a >> \sigma_c > \sigma_b$, and the corresponding thermoelectric power values are [3] -59, +1.5 and -49.5, all $\mu V\ K^{-1}$. By comparison, the room temperature thermopower for a

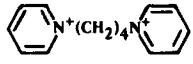
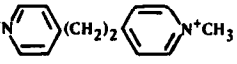
compressed disc of $(DEBP)^{2+}(TCNQ)_4^{2-}$ was -440 μV K^{-1}, and similar high negative RT thermopowers were found for three other semiconducting complexes[4]. For $(DEBP)^{2+}(TCNQ)^{2-}$ the electron mobility μ_e of 10-25 cm^2 V^{-1} s^{-1} at RT ($\alpha T^{-1.6}$) and hole mobility μ_p of 4-8 cm^2 V^{-1} s^{-1} ($\alpha T^{-1.1}$) were taken to indicate narrow band conduction, with scattering by lattice phonons.

EXPERIMENTAL

The two complexes studied are shown in Table 1.

Table 1

Crystallographic Data

	Complex I	Complex II
Formula	$DPB^{2+}(TCNQ)_4^{2-}$	$DMPA^{2+}(TCNQ)_4^{2-}$
Cation		
	Dipyridyl butane	Dimethyl-bipyridinium ethane
Crystal.	Triclinic	Triclinic
Axis, &	b, short	b, short
Crystal	a, medium*	a, long
edge	c, long*	c, medium
TCNQ	dimers along [110]	pairs of dimers along [110]
Stack	at acute angle to b	at acute angle to b

* There is a second habit, hexagonal faces in the ac plane, where the external crystal dimensions may be apparently reversed, G.A. Owens[5] c is the direction at 1 to planes of TCNQ's and cations.

The preparative and analytical methods have been summarised in an earlier review[4]. Crystals of (I) were prepared by slow cooling of a nearly boiling acetonitrile-water solution over three days in a Dewar flask of hot water. Crystals of (II) were prepared by diffusion in a thermal gradient of 18-11°C over 3 months,

the solvent being dry analar acetone. The conductivity determination used 2 copper wires attached by Ag-paint to the opposite sides of single crystals, in glass cells first pumped to 10^{-6} torr and filled with 10 torr He gas for heat transfer. The single crystal thermopower equipment will be described in a later paper.

RESULTS AND DISCUSSION

In the case of I, DPB $(TCNQ)_4$, the data presented are the average values of measurements on several crystals picked from three batches, and are believed to be accurate within 10%. All the logσ vs T^{-1} graphs exhibited two linear branches separated by a region of lower slope ("plateau"). A typical example is shown in Fig 1. For all 3 axes the transition occurred in the same temperature interval 255-330 K. The conductivity and thermoelectric power values for all 3 axes of complex I and complex II are shown in Table 2. In the case of complex II, as shown in Fig II, there is only a very small interval of lowest slope, this occurring around 273 K for all 3 crystal axes. The low temperature and high temperature activation energies are respectively 0.19 and 0.32 eV.

Table 2

Electrical Anisotropy

Complex I	Complex II
σ_a (400K, 200K) 4.9×10^{-1}, 5.0×10^{-3}	σ_a (300K) 0.6×10^{-1}
σ_b (400K, 220K) 5.7×10^{-1}, 7.3×10^{-3}	σ_b (300K) 1.8×10^{-1}
σ_c (400K, 220K) 4.5×10^{-2}, 4.9×10^{-4}	σ_c (300K) 0.26×10^{-1}
Q_a (400K, 220K) -775, -219	Q_a (300K) -600
Q_b (400K, 220K) -648, -170	Q_b (300K) -600
Q_c (400K, 220K) -546, -248	Q_c (300K) -280

$\sigma, \Omega^{-1}\,m^{-1}$; $Q, \mu V\,K^{-1}$

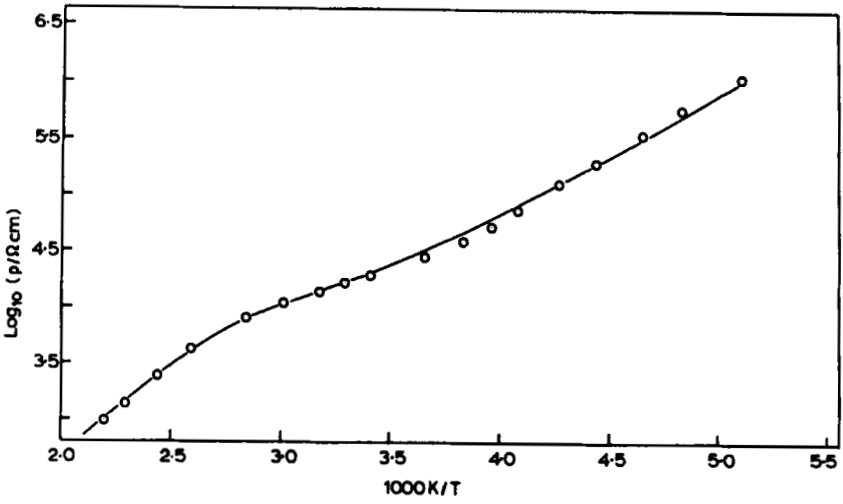


FIGURE 1 Resistivity ρ (Ω cm) - temperature for the a (medium) axis of DPB(TCNQ)$_4$ single crystal. The line is the computerised fit with the parameters listed in Fig 3.

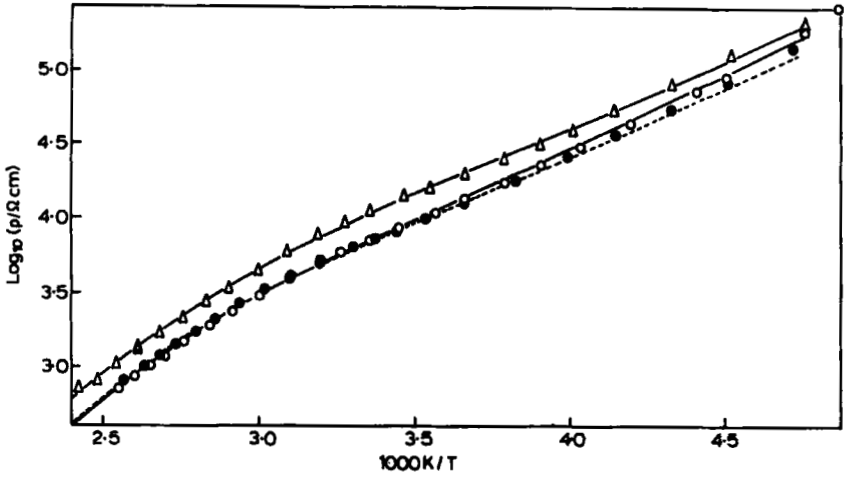


FIGURE 2 Resistivity ρ - temperature for the c(medium) axis of DMPA(TCNQ)$_4$. O evacuated at 90°C, ● 104°C, Δ a second specimen evacuated at 100°C. Lines are computerised fits.

The results show the conductivity in the ab plane is 5-10 times higher than in the c direction, across the alternate planes of cations and anions. This agrees with our earlier work on $(DEBP)(TCNQ)_4$ and other complexes.[4] There is a higher conductivity along the TCNQ stacks $\sigma = 740\ \Omega^{-1}\ m^{-1}$ for TEA $(TCNQ)_2$. This complex also has as much higher anisotropy, suggesting a higher degree of order in these crystals. The presence of disorder in our two complexes appears to be confirmed by an analysis of the temperature-coefficient behaviour.

Temperature Coefficient of Conductivity

Roberts and Schmidlin have given a statistical treatment of the effect of localised electron and hole states in the band-gap, on the conductivity of semiconductors,[6] successful in accounting for graphs like Fig 1 when found for Ge and Si, and Fig 2, when found for GaAs.[7] In the model we have energy levels, conduction band edge E_c, deep lying localised electron levels E_m and localised hole levels E_q in the gap, and valence band edge E_v. The respective densities of states, in m^{-3}, are N_c, N_m, N_q and N_v. We take $E_v = 0$, and assume $N_c = N_v = 2.5 \times 10^{25}\ m^{-3}$ and then take the given rules[6,7] to obtain initial estimates of E_c, E_m, E_q, N_m, using the three apparent activation energies clearly defined in Fig 1 for complex I (less clear for II). An important guideline is that the thermopower establishes the complexes to be N-type over the whole temperature range embracing the transitions. Thus we assume the high temperature activation energy $E_3 \approx (E_c - E_v)/2$, and if E_1 is the low temperature activation energy, E_2, the intermediate value $E_1 - E_2 = \frac{1}{2}(E_c - E_m)$ and $E_2 - E_3 \approx \frac{1}{2}(E_v - E_q)$. If the transition temperatures are T_{12} and T_{23} in order $T_1 < T_2 < T_3$, $N_m = N_c \exp (E_m - E_c)/kT_{12}$, $N_q = N_v \exp (E_v - E_q)/kT_{23}$. The partition functions for electrons Φ_e and holes Φ_p were calculated and hence the Fermi level $E_F = \frac{kT}{2} \ln \frac{\Phi_p}{\Phi_e}$

Thereafter, to simplify the programme it was necessary to omit the hole contribution to the conductivity σ, ie to assume the mobility $\mu_e >> \mu_p$, although in earlier work on similar compounds, $\mu_e \sim 3\mu_p$. With this assumption, ie

$$\sigma = AN_c \exp (E_F - E_c)/kT \text{ where } A = e\mu_e,$$

the parameters E_1, A, N_m, N_q and E_c were varied to give the best fit to the logσ vs T^{-1} plot, Figs 1 and 2, where examples are given. Typically, as in Fig 2 all our computed values lie within 3% of the observed values for temperatures above 210 K. The details of our procedure must be reserved for a further publication. Applying this method to the three crystal axes of $DPB(TCNQ)_4$ gives the energy level scheme in Fig 3a, and to $DMPA(TCNQ)_4$ in Fig 3b. The dotted levels for the b axis of the lattice show the maximum variability noted between crystals. Applying the Lark-Horowitz[8] equation for a band theory semiconductor to a calculation of thermopower Q, and assuming $\mu_e/\mu_p >> 1$, gives negative values, of course, with the correct temperature coefficient, but some 900 $\mu V\ K^{-1}$ more negative than observed. It seems pretty clear that we have neglected the hole contribution to the thermopower, and hence to the conductivity, so in future work an attempt to omit this simplifying assumption will be necessary.

CONCLUSIONS

Since there is every reason to assume an isotropic band gap, then the higher values for the a and c axes (if not due to variations from crystal to crystal) might imply activated mobilities contributing to the activation energies along these axes, and neglected in the analysis. It must also be noted however, that $E_c - E_v$ is deduced from an experimental slope E_3 covering a small number of points at the highest temperature, so inaccuracies can arise from this factor. The densities of states for (I) appear very reasonable, whereas for (II) those for the localised electron levels, N_m, seem very high. Even for (I), the values of N_m and N_q seem too high to arise simply from any chemical impurities present, and structural disorder must also be assumed present. Similar complexes have given evidence for considerable disorder in ac conduction,[9] and in the heavy trapping of photoconductive pulses, which fit the Mort-Scher treatment[10]. The densities of Curie law spins also point to disorder, viz 3.7×10^{21} for (I), and 5.2×10^{21} for (II), admittedly on different crystal preparations.

By rapid crystallisation it was possible to prepare microcrystals or "hairs" of a more highly conducting (very low activation energy) phase of $(DMPA)^{2+}\ (TCNQ)_4^{2-}$.

X-ray crystallography (Dr S C Wallwork) shows this to be even more disordered, and the higher conductivity may reflect the onset of a hopping conduction between states in the band gap.[11]

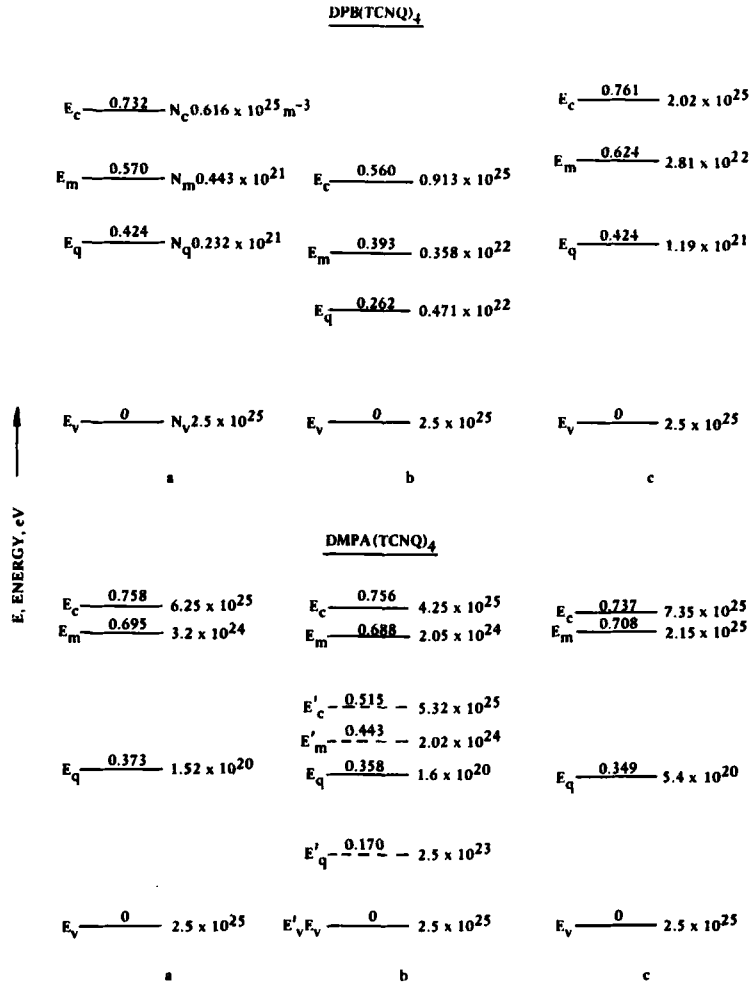


FIGURE 3 Energy levels and state densities, a, b and c axes.

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