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Band Structure of DEBP(TCNQ)$_4$

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Synopsis. Band structure calculations are reported for the intermediate conducting complex salt, DEBP(TCNQ)$_4$ (DEBP: *N,N'*-diethyl-4,4'-bipyridinium, TCNQ: tetracyanoquinodimethane). They show that the array of TCNQs forms a two-dimensional band structure with conduction and valence band widths 0.1 and 0.03 eV respectively. Conduction in the third direction is likely to be by hopping or tunnelling. The results are consistent with the experimental observations of electrical conductivity, magnetic susceptibility and thermoelectric power.

TCNQ complex salts have been extensively studied to explore the relationship between structure and properties. The series of general formula R^{2+}-$(\mathrm{TCNQ})_n^{2-}$, where $2<n<5$ and R^{2+} is an organic dication, has been investigated in some detail and a wide range of electrical and magnetic behaviour reported.[1—4] The complex salt DEBP(TCNQ)$_4$ displays intermediate conductivity and is typical of this group of materials (Table 1). It is a semiconductor with a band gap of 0.5 eV, and the anisotropy of conductivity is qualitatively consistent with the crystal structure. Assuming the application of band theory, the mobilities of electrons and holes have been deduced from an analysis of thermoelectric power measurements.[2] Alternating current conductivity studies reveal a significant concentration of localized states resulting from crystal imperfections.[4] Magnetic measurements are consistent with a thermally accessible localized triplet state, and also indicate the presence of a significant concentration of imperfections.[3]

In this paper, band structure calculations are reported in an attempt to provide a more quantitative relationship between structure and properties.

Table 1. Summary of Electrical and Magnetic Properties

(A) Single crystal conductivity

Axis	Conductivity/ S cm^{-1}	E_A (260 K)/eV
a	1.2×10^{-4}	0.25
b	2.5×10^{-3}	0.28
c	3.2×10^{-3}	0.27

(B) Carrier mobility
Seebeck effect shows,
μ_e=10—25 cm^{2}V^{-1}s^{-1}, μ_h=4—8 cm^{2}V^{-1}s^{-1}
in intrinsic region, assuming 3-D band theory and $m^*=m$,

(C) E.S.R. intensity varies as

$$I \propto \frac{1}{T(3+\exp(J/k_BT))}$$

with J=0.075 eV.

(D) Indications of defect concentration
- (i) Curie component of magnetic susceptivility gives 1.6×10^{22} spins per mole
- (ii) Alternating current conductivity gives density of localized states at Fermi level as 1.3×10^{25} m^{-3}

Band Calculation

X-Ray crystallography shows that the TCNQ molecules are stacked plane to plane in groups of four along the b-axis (Fig. 1),[2] giving rise to a two-dimensional molecular lattice in the bc plane. The tetrad carries two negative charges which are evenly distributed over the four molecules. The dications lie between the conduction planes of the TCNQ molecules (Fig. 2).

The band structure calculation uses the tight-binding approximation based on the extended Hückel method and is similar to that of Whangbo and Hoffmann.[5] The programming details are described elsewhere.[6] Firstly the molecular wave functions for

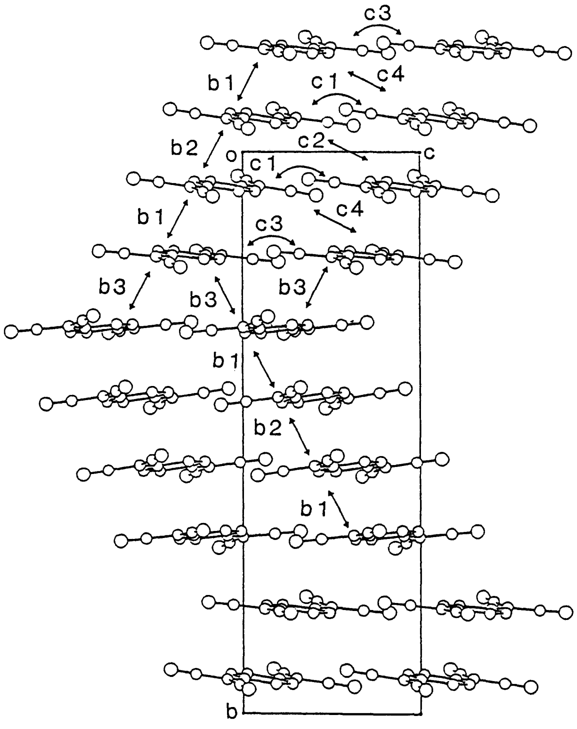

Fig. 1. The crystal structure of DEBP(TCNQ)$_4$ showing the interactions in the bc plane.

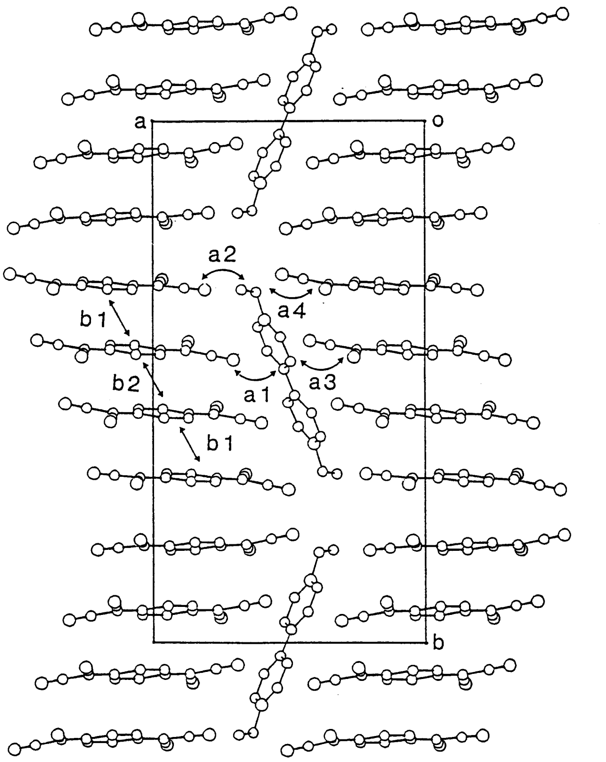

Fig. 2. The crystal structure of DEBP(TCNQ)$_4$ showing the interactions between the cation and the TCNQ tetrad, as well as within the tetrad.

Table 2. Transfer Integrals t/eV

(a) Within the TCNQ sheet			
bl	0.176	cl	0.1×10^{-3}
b2	0.194	c2	1.4×10^{-3}
b3	0.038	c3	0.2×10^{-3}
		c4	1.4×10^{-3}
(b) Between cation and TCNQ sheet			
al, a2, a3, a4	$<10^{-4}$		

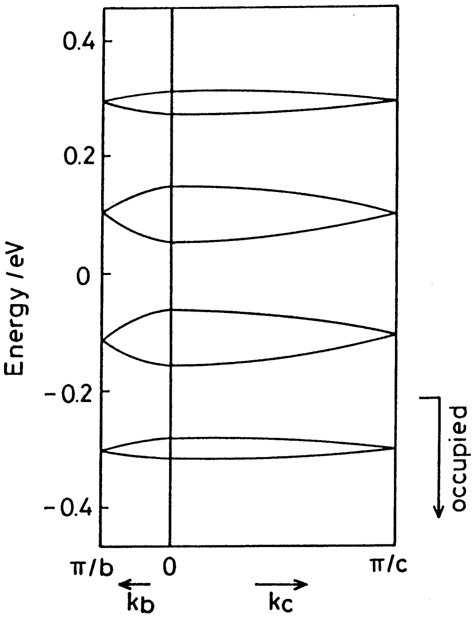

Fig. 3. The band structure of DEBP(TCNQ)$_4$.

the TCNQ molecules were calculated using the experimentally determined atomic positions. The various nearest neighbours overlap integrals (S) relevant to conduction, shown in Fig. 1 as b1, b2, b3, c1, c2, c3, and c4, were then calculated and the transfer integrals were obtained assuming proportionality to overlap integrals,

$$t = KS \tag{1}$$

where K is taken as -10 eV.[7]

Similarly, the molecular orbitals of the cation were calculated and the transfer integrals between cation and the nearest TCNQ molecules were estimated using second order perturbation theory because of the large energy difference.

The absolute values of the transfer integrals are listed in Table 2. Knowing the transfer integrals the band structure was calculated (Fig. 3). The interactions split the LUMO of TCNQ (or the HOMO of TCNQ$^-$) into four bands, the lowest of which is filled and the others empty at 0 K.

Results and Discussion

Dimensionality. From the values of the transfer integrals it is clear that interaction within the tetrad is nearly uniform (bl=b2), and that the most significant interaction between tetrads which determines the conduction path , is b3. By comparison, the transfer integrals between any of the TCNQ s in the tetrads and the cation (al—a4) are negligible. The material can therefore be represented, to a good approximation, by a two-dimensional band structure. Furthermore, since the band width is determined by the transfer integral corresponding to b3, the conductivity in the b and c directions should be equivalent, which is in good agreement with the experimental observations (Table 1).

Band Conduction. The band calculation shows the material to be a semiconductor. The one-electron calculation gives a separation between the bands of 0.1 eV but allowance must be made for Coulomb interaction between the electrons to obtain the true band gap (E_g). It has been suggested that for a two-dimensional system,[3] the band gap is given by

$$2E_A = E_g = (U - 8t), \tag{2}$$

where t is identified with the average interaction. By taking U to be 1.5 eV, as proposed by Tanaka,[8] then E_g=0.5 eV, in good agreement with experiment.

The band widths calculated for the conduction band of 0.1 eV and for the valence band of 0.03 eV are well within the criterion for band conduction and since the band widths are both greater than k_BT (0.025 eV at room temperature), just satisfy the criterion for broad band conduction.[9] The greater width of the conduction band indicates that the electron has the higher mobility, in agreement with experiment (Table 1).

Conduction in the a Direction. Conduction in the direction normal to the two-dimensional array of TCNQs is clearly not band conduction, as the small transfer integral would lead to far too narrow a band. A likely mechanism is hopping or tunnelling of the carriers via the cation. This is supported by the observation that the conductivity is lower in this direction by an order of magnitude, whilst the activation energy is isotropic within experimental error, indicating a low hopping barrier. When the carrier is an electron, the intermediate species formed is the resonance stabilized monocation, which corresponds to the violet species readily formed in solution.10) In contrast, for methyltriphenylphosphonium$(TCNQ)_4$, which does not form such a stabilized intermediate, the anisotropy is two orders of magnitude greater.11)

Thermoelectric Power. The band calculations give some insight into the validity of the assumptions made earlier in the analysis of the thermoelectric power measurements to derive electron and hole mobilities and their temperature dependencies.2) The assumption of band conduction is clearly valid, but a two-dimensional density of states with allowance for the number of TCNQ sheets per unit cross section, might have been more appropriate. However, the significant concentration of imperfections tends to shift the density of states towards the three-dimensional value, so the error is likely to be small. No information was available on electron and hole effective masses so they were assumed to be approximately equal to the free electron mass. The calculated band widths enable the effective masses to be estimated from,9)

$$m = \frac{\hbar}{Wa^2}, \tag{3}$$

where W is the band width and a the lattice constant. The value of m is clearly strongly dependent on the value of a which is not obvious for such a complex structure. If we regard the TCNQ tetrad, over which the electronic charges are fully delocalized, as the basic structural unit, then the repeat distance is 7—13 Å depending on the direction chosen. This gives $m_e/m=0.5$ to 1.6 and $m_h/m=1.5$ to 5, suggesting that equating the carrier masses with the free electron mass is a fair approximation.

Magnetic Properties. Since the intra-tetrad transfer integrals are much greater than those between tetrads, temperature dependent paramagnetism associated with the thermal population of a low lying triplet state is to be expected. The singlet triplet splitting is given by8)

$$J = \frac{4t^2}{U}. \tag{4}$$

Taking the average transfer integral within the tetrad and $U=1.5$ eV, then $J=0.088$ eV, in reasonable agreement with the experimental value (Table 1).

Conclusion

The satisfactory agreement between theory and experiment provides strong support for the two-dimensional band model adopted for this group of compounds.

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