OPTICAL ABSORPTION IN "QUARTER-FILLED BAND" TCNQ SALTS

D.B. TANNER(a,b), Ivar HAMBERG(a), C.S. JACOBSEN(b), M. ALMEIDA(c), K. CARNEIRO(d),
A.J. EPSTEIN(e), and Joel S. MILLER(f)

a) University of Florida, Gainesville, FL 32611 USA
b) Physics Laboratory III, Technical Univ. of Denmark, DK-2800 Lyngby, Denmark
c) Department of Chemistry, LNETI, P-2686 Lisbon, Portugal
d) Physics Laboratory I, Univ. of Copenhagen, DK-2100 Copenhagen, Denmark
e) Ohio State University, Columbus OH 43210, USA
f) du Pont Experimental Station, Wilmington, DE 19898, USA

We have studied the infrared and optical properties of a group of TCNQ salts which contain on
average 0.5 electrons per TCNQ: $MTPP(TCNQ)_2$, $MNEB(TCNQ)_2$, and $(NMP)_x(Phen)_{1-x}TCNQ$. In the
cases of $MTPP(TCNQ)_2$ and $MNEB(TCNQ)_2$ the crystals were sufficiently large that spectra could
be obtained from up to six different crystallographic faces. The spectra are complicated by
the presence of a strong localized exciton (observed for most polarization directions) in the
energy range where the charge-transfer excitation from anion to anion occurs. The charge
transfer excitation is present but rather weak. These results are compared with calculations
using an extended Hubbard model of short chains and small rings.

1. INTRODUCTION

In this paper we describe the optical spectra
of "quarter-filled band" tetracyanoquinodimeth-
anide (TCNQ) salts, i.e., those with on average
half an electron per TCNQ molecule, and describe
calculations for the simplest extended Hubbard
model which could apply to these materials:
two electrons on four sites.

The materials which we have studied are
$MNEB(TCNQ)_2$, $MTPP(TCNQ)_2$, and
$NMP_x(phen)_{1-x}TCNQ$ with x near 0.5. Here MNEB
is methyl N-ethyl benzimidazolium, MTPP is methyl
triphenyl phosphonium, NMP is N-methyl phena-
zinium, and phen is phenazine. In $NMP_{0.5}$
$(phen)_{0.5}TCNQ$, the NMP donor ions and neutral
phen molecules alternate in the donor chain; for
x>0.5, additional NMP ions replace phen molecules.
The TCNQ molecules are almost uniformly spaced
along the chain.[1] In contrast, the TCNQ chains
in $MTPP(TCNQ)_2$ and $MNEB(TCNQ)_2$ have suffered
(even at room temperature) severe structural
distortions.[2,3] $MTPP(TCNQ)_2$ has been studied
previously,[4,5] as has $MNEB(TCNQ)_2$ in the
infrared.[6]

2. EXPERIMENTAL DETAILS

The materials were prepared using techniques
already described.[7,8] The $MTPP(TCNQ)_2$ and
$MNEB(TCNQ)_2$ crystals were sufficiently large
that the reflectance could be measured on up to
six different facets. Kramers-Kronig analysis
give the optical functions, such as the frequency
dependent conductivity.

Unpolarized transmission measurements on
$NMP_x(phen)_{1-x}TCNQ$ powders embedded in KCl gave
the absorption coefficient of the KCl pellet;
division by the volume fraction yielded the
direction-averaged absorption.

3. RESULTS

Fig. 1 shows the absorption coefficient of
four $(NMP)_x(phen)_{1-x}TCNQ$ samples with x=0.49,
0.53, 0.55, and 0.59. Five prominent peaks
(marked A-E) are seen, at frequencies A=3500
cm^{-1}/0.4 ev, B=10,000 cm^{-1}/1.2 eV, C=16,000
cm^{-1}/2.0 eV, D=28,000 cm^{-1}/3.4 eV, and E=40,000
cm^{-1}/5.0 eV. These peaks are most distinct in
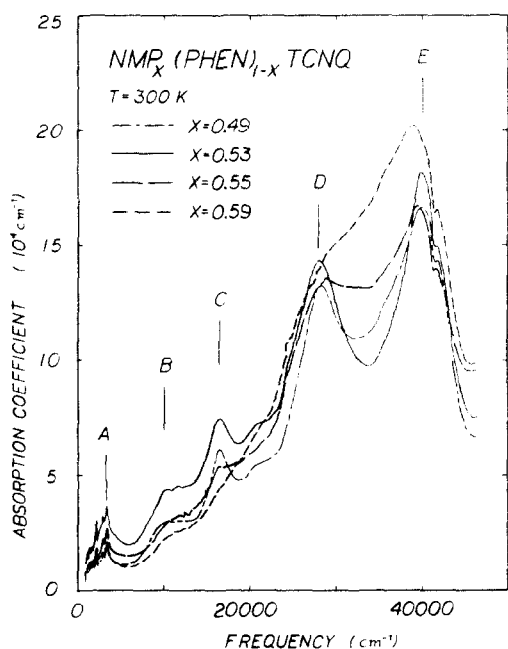the x=0.49 and 0.53 samples and become much less
distinct with increasing x.

FIGURE 1

(NMP)$_x$(phen)$_{1-x}$TCNQ absorption coefficient.

FIGURE 2

Frequency-dependent conductivity of MTPP(TCNQ)$_2$

Fig. 2 shows the frequency-dependent conductivity of MTPP(TCNQ)$_2$ for two polarizations. [010] is the chain-axis direction while [101] is a direction close to the TCNQ long axis.[2] Peaks A and B are the dominant features in the chain-axis spectrum; C and D in the long-axis one.

Fig. 3 shows the conductivity of MNEB(TCNQ)$_2$ for four polarizations, taken on two different crystallographic faces. In this crystal,[3] [001] is the chain axis direction while a* is perpendicular to the chain axis and nearly along the TCNQ long axis. [100] is also nearly along the long axis and (on account of the monoclinic crystal structure) has a significant chain-axis component. Finally, [021] is nearly perpendicular both to the chain and to the TCNQ long axis. Peak A is seen only in the chain-axis; C only in the TCNQ long axis; B is seen in both directions.
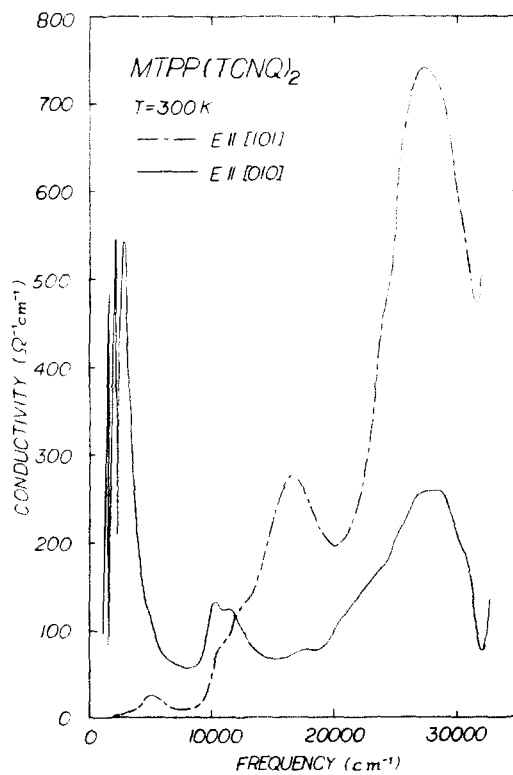
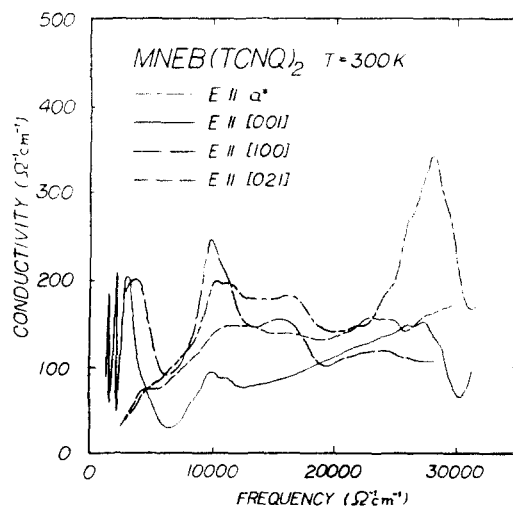FIGURE 3

Frequency-dependent conductivity of MNEB(TCNQ)

4. DISCUSSION

A large-U Hubbard model seems appropriate for discussing the properties of these compounds.

We have solved the extended Hubbard model[9,10] for the simplest system possible, two electrons occupying four sites, with periodic boundary conditions. We used a Hamiltonian which includes t, the transfer integral, U, the on-site Coulomb repulsion, V_1, the Coulomb interaction of electrons on adjacent sites, and V_2, the second-neighbor Coulomb term.

The single t wave functions are of three types,

$$|\uparrow\downarrow, 0, 0, 0\rangle \qquad \text{on site,}$$
$$|\uparrow, \downarrow, 0, 0\rangle \qquad \text{"2k}_F\text{"}$$
$$|\uparrow, 0, \downarrow, 0\rangle \qquad \text{"4k}_F\text{"}$$

where "$2k_F$" and "$4k_F$" identify the charge-density variation in terms of the Fermi surface of non-interacting electrons.

For large U, the ground state contains mostly $2k_F$ and $4k_F$ terms, with a small admixture of on-site terms as well. For small t, either $4k_F$ or $2k_F$ configurations dominate,[9] depending on whether V_1 is larger or smaller than $2V_2$. At t becomes larger, the $2k_F$ configuration becomes more significant especially if V_1 and $2V_2$ nearly are equal.

There are two charge-transfer excitations in this model. CT1 is governed by t and V_1-2V_2. CT2 is governed by t and $U-V_1$.

The common interpretation[11,4] of the spectra of these compounds would be that peaks A and B are CT1 and CT2, C, and D are localized excitons LE1, LE2, etc. of TCNQ. The problem, as pointed out by Yakushi et al,[5] is that isolated TCNQ ions have LE1(-) at the location of peak B with a characteristic vibronic splitting such as is observed in Figs. 2 and 3. The assignment of B entirely to LE1, however leaves no good explanation for peak C; in addition, our ring tetramer calculation finds CT2 should be in the vicinity of peak B, although with a rather low oscillator strength.

The answer is probably related to the complex ground state of the TCNQ chain. For example, if there is a strong $4k_F$ charge-density variation, then the chain consists of alternating ions and neutral molecules. The spectrum should show the exciton of both species LE1(-), peak B, and LE1(0), at[4] 24,000 cm^{-1}/3 eV. If the configuration contains significant amounts of both $4k_F$ and $2k_F$ configurations, then the spectrum should show both the exciton of the isolated ion, LE1(-), peak B, and the exciton of the dimer, LE1(-,-), peak C.

To verify this conjecture, it would be necessary to include in the four-site model not only the two electrons sharing the highest occupied level but also the eight electrons (two per TCNQ) in the next lower one.

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