Electrical transport properties of morpholinium-TCNQ2 compounds

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ELECTRICAL TRANSPORT PROPERTIES OF MORPHOLINIUM-TCNQ₂ COMPOUNDS

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Measurements of the frequency and electric field dependence of several low-dimensional semiconductors, belonging to the class of substituted morpholinium-TCNQ₂ compounds, are presented. Large enhancement of the conductivity is seen at frequencies in the MHz region and at electric fields of 1 to 10 V/cm. An empirical description is given in terms of field (or frequency) activated contributions to the conductivity. It is shown that the functional form of the frequency and field dependence is related to the degree of disorder that is present in the system. The systems should be viewed as disordered conductors (similar to Qn-TCNQ₂), rather than as semiconductors.

1. Introduction

XY-substituted morpholinium bis-tetra-cyanoquinodimethane (XY(T)M-TCNQ₂), where X, Y are alkylgroups, form a class of quasi one-dimensional (semi-) conductors with a quarter-filled valence band*. Due to the large electron-electron interaction ($U \approx 1.4$ eV), which exceeds the band width of the electron bands (W , typically 0.5 eV) one can justifiably take the $U \rightarrow \infty$ limit of the Hubbard model where the band is effectively half-filled and the eigenstates have lost their spin-degeneracy. For most systems the transfer integrals that couple the valence orbitals on adjacent TCNQ molecules have been calculated by Van Smaalen and Kommandeur [1]. The correspondence between the calculated gaps and the observed activation energies for the conduction process is not very satisfying. However, considerable improvement is obtained if one incorporates the effect of thermal expansion on the transfer integrals as was done by

Oostra [2]. This single-particle theory may be of help in the explanation of the activation energies but it fails to explain the peculiarities that accompany electron transport in these compounds such as the shot-noise components in the noise-spectrum observed by Jos et al. [3–5] and the field and frequency dependence of the conductivity (this paper and [6, 7]). The noise measurements led Jos et al. to propose that solitons with fractional charge $\frac{1}{2}$ are the charge carriers in these systems. Against this soliton picture there are serious objections, which we will outline at the end of the discussion.

In this paper we study non-linearities in the conduction process in a large number of different compounds. It appears that the form of the non-linearities is influenced by *disorder*, although the non-linearities are still present when static (or quasi-static) disorder is absent. Non-linearities are usually found in systems with a small activation energy ($E_a < 0.1$ eV) and/or disordered donor systems. In the discussion we will argue that in these cases the gap is effectively filled with localized states, created by either static or dynamic (thermal) disorder of the lattice. This leads to the conclusion that the elec-

* The following abbreviations are used for the substitutions:
H = hydrogen, M = methyl, E = ethyl, P = propyl, iP = isopropyl and B = buthyl.

tronic structure of some M-TCNQ₂ compounds is in many respects similar to that of the disordered metal Quinolinium-TCNQ₂ (Qn-TCNQ₂) for which the same field and frequency effects have been observed.

2. Experimental

All measurements were performed on single crystals obtained by slow cooling of an acetonitril solution of the constituents. The crystals had typical dimensions of $5 \times 1 \times 0.2 \text{ mm}^3$. In all measurements, silver paint was used to obtain electrical contact. Usually a two-probe configuration was employed, while checks were made on the contact linearity using a four-probe method. This showed that the contact resistance was negligible. The high-field measurements were done with pulsed electric fields in order to eliminate Joule heating of the sample. The high-frequency measurements, over the range of 4–2600 MHz, were made using a Hewlett Packard 8754A network analyzer with a 8502A reflection/transmission test set. In the experiments the crystal was mounted at the end of a 50 Ω coaxial lead. The measurement of the phase and amplitude of the signal, that is reflected off the sample, allows one to calculate the complex conductivity of the sample. Unless stated otherwise, the results refer to measurements at room temperature, with an electric field along the TCNQ stacking axis. We did not succeed in extending the frequency dependent measurements to other temperatures than room temperature, due to the extreme fragility of the crystals.

3. Results and analysis

All compounds studied in this paper are one-dimensional, i.e. the conductivity in the directions parallel and perpendicular to the TCNQ-chain differs by a few orders of magnitude. The electric field dependence of the conductivity is also highly anisotropic. Fig. 1 shows the directional dependence of the field-dependent conductivity of METM-TCNQ₂. For an electric field

Fig. 1. Field dependence of the conductivity of METM-TCNQ₂ along three principal axes at room temperature. The conductivity is scaled to the zero-field value: $10 (\Omega\text{cm})^{-1}$ for $E||c$ and 100–1000 times less for $E\perp c$ (c is the TCNQ stacking axis).

along the TCNQ-chain, which coincides with the length direction of the needle shaped crystals, the effect is about 100 times stronger than for electric fields that are perpendicular to the TCNQ-spine. For several samples that exhibit nonlinear conduction, the temperature dependence was measured and it was found that (in the absence of phase transitions) the behaviour could be represented by

$$\sigma(E, T) = \sigma(E, T_0) \exp \left[-E_a \left(\frac{1}{T} - \frac{1}{T_0} \right) \right], \quad (3.1)$$

where σ is the conductivity, which is a function of both the temperature (T) and the electric field (E). The activation energies (E_a) are in accordance with previously reported values [8]. An important feature of eq. (3.1) is that the field-dependence of the normalized conductivity $\sigma(E, T)/\sigma(0, T)$ does not depend on temperature. From this one may infer that there is just a single conduction process, in contrast with the situation in charge density wave (CDW) systems. In the latter case the field and frequency dependent part of the conductivity are due to the sliding motion of a CDW, whereas the linear part of the conductivity is due to single-particle conduction [9].

For our samples the field dependence of the

conductivity appears to be represented by the empirical function

$$\frac{\sigma(E, T)}{\sigma(0, T)} = 1 + A_E \exp \left[- \left(\frac{E_0}{E} \right)^{\alpha_E} \right]. \quad (3.2)$$

Similarly, the frequency dependence is described by

$$\frac{\sigma(\omega, T)}{\sigma(0, T)} = 1 + A_\omega \exp \left[- \left(\frac{\omega_0}{\omega} \right)^{\alpha_\omega} \right], \quad (3.3)$$

where α_E and α_ω are the major empirical parameters. Table I lists the parameters A and α for various samples as obtained from a fit to the data presented in fig. 2. For α equals 1, the excess conductivity is "activated" by field (or frequency) in the same way as the conduction of a semiconductor is activated by temperature. We will therefore refer to this conductivity as being activated by field and frequency. This behaviour is found e.g. with Zener tunneling [10] and was initially used in the empirical description of the

Fig. 2. Dependence of the conductivity of some XY(T)M-TCNQ₂ compounds on frequency (left) and electric field (right). The drawn lines are fits to eqs. (3.3) and (3.2) respectively.

Table I
Conductivity parameters of XY(T)M-TCNQ₂

Donor group	E_g (eV)	Disorder [2]	Frequency		Electric field	
			A_ω	α_ω	A_E	α_E
MEM	0.23	no	no effect		no effect	
MEM (350 K)	0.0	yes	—	—	4.8	0.28
MEM ₈₄ METM ₁₆	0.1	yes	>20	0.11	>5	0.15
METM	0.07	see text	3.9	0.49	1.7	0.50
Qn (40 K) [13]	0.03	yes	—	—	0.43	0.52
Qn (80 K) [14]	0.03	yes	1.1	0.6	—	—
MBM [7]	0.07	yes	—	—	large effect	
MBTM	0.0	yes	1.5	0.41	1.1	0.33
HBM	0.13	—	8.0	0.48	2.4	0.45
HBMT [7]	0.11	yes	—	—	some effect	
HEM	0.39	yes	1.3	0.22	small effect	
HiPM	0.22	—	5.0	0.71	small effect	
PiPM	?	—	no effect		no effect	
EiPM	0.31	—	no effect		no effect	
DMM	0.30	no	—	—	no effect	

field induced depinning of charge density waves (CDW) [11]. A value of $\alpha < 1$ can be interpreted as arising from a distribution of depinning potentials (or frequencies)*. The field-induced part of the conductivity is the Laplace transform of the pinning potential distribution $P_\alpha(E_d)$

$$A_E \exp \left[- \left(\frac{E_0}{E} \right)^\alpha \right] = \int_0^\infty dE_d P_\alpha(E_d) \times \exp \left[- \left(\frac{E_d}{E} \right) \right]. \quad (3.4)$$

For $\alpha = 1$ one has that $P_\alpha(E) = \delta(E - E_0)$, corresponding to a single depinning potential; if $\alpha < 1$, there is a distribution of depinning potentials, which broadens as α is lowered. For $\alpha = \frac{1}{2}$ the distribution is of the form

$$P_{1/2}(E_d) \propto E_d^{-3/2} \exp \left(- \frac{E_0}{4E_d} \right) \quad (3.5)$$

and for $\alpha \leq 0.2$ the distribution of pinning potentials is almost flat and the conductivity increases linearly in the field.

The conclusion that a distribution of elementary processes is activated by field and frequency is supported by the measurement of the frequency dependence of the complex conductivity

$$\sigma(\omega) = \sigma'(\omega) + i\sigma''(\omega). \quad (3.6)$$

The results can be plotted in a Cole-Cole plot, i.e. σ' vs. σ'' [12]. In such a plot a single relaxation time produces a semicircle. A superposition of processes with different relaxation times gives rise to the more elongated curves that are observed in our samples (see fig. 3).

From table 1 one may divide the compounds into two classes. The first class is characterized by:

- (1) a low room-temperature conductivity ($\ll 1 (\Omega \text{ cm})^{-1}$) and high activation energy ($> 0.1 \text{ eV}$),
- (2) an ordered donor system,

*The reader should for the remainder of this section keep in mind that wherever we use depinning potential, one may also read depinning frequency.

Fig. 3. Cole-Cole plots of the frequency dependence of the complex conductivity of four morpholinium-TCNQ₂ salts between 0 and 2600 MHz. The filled squares correspond (clock-wise) to frequencies of 0, 26, 90, 300 and 1200 MHz.

- (3) a field and frequency independent conductivity.

For the second class one has:

- (1) a room temperature conductivity of the order of $1 (\Omega \text{ cm})^{-1}$ and an activation energy that is below 0.1 eV,
- (2) a usually disordered donor system (the disorder may be either static or dynamic),
- (3) a very strong dependence of the conductivity on electric field and frequency (also, the field and frequency dependences are similar).

In the discussion we will turn to the possible origin of this distinction and try to answer the question why the non-linearities are only observed in small-gap semiconductors. Furthermore, we will study the correlation of the empirical parameter α with possible sources of disorder.

Finally, it is worthwhile to note that the frequency and field dependence of most compounds are remarkably similar. For those compounds where both the field and frequency dependence could be measured, one finds that α_ω and α_E are almost the same. The frequency-effect is in all cases larger than the field-effect. Such a correspondence between field and frequency dependence has also been found in CDW-systems [9]. In the more closely related case of Qn-TCNQ₂ this correspondence also exists [13, 14], but has, to our knowledge, so far been left unexplained.

4. Discussion

As shown above on basis of their non-linear transport properties, the investigated TCNQ-compounds can be grouped into two classes. In this section we will try to explain the origin and link the experimental observations of non-linear transport to the electronic structure of the systems. To this end we shall consider specifically the series $\text{MEM}_{1-x}\text{METM}_x\text{TCNQ}_2$. This series is best suited to study the influence of disorder on the field and frequency dependence of the electrical conductivity. Thereafter, we will consider the class of non-linear conductors as a whole and argue that in the low-gap semiconductors (dynamic) disorder is important.

It is useful at this stage to discriminate between static and dynamic disorder. The disorder, that is of our concern here, is the randomness of the parameters that describe the electronic system, i.e. either the transfer integrals or the local potentials. The on-site potentials may be randomized by orientational disorder of the dipolar moments of the donor molecules. Whether or not this disorder is static or dynamic is irrelevant as long as the time scale of canting of the donor dipolar moments is long compared to the time scale of electron motion. We will refer to this donor-induced disorder as (semi)static disorder. Another source of randomization of the electron system is the large thermal vibration of the anions (typically $0.2 \text{ \AA}$ [15,16]). In combination with the sensitivity of the transfer integral with respect to molecular displacements*, this leads to a spread of 30 to 40% in the values of the transfer integrals. This disorder is dynamic and changes on the phonon time scale, which is again long compared to the time scale of electron motion. The effect of this type of disorder was the subject of a paper by the authors [18], where it was applied to other synthetic semiconductors and was seen to be of particular relevance when the gap is small compared to the bandwidth.

* We estimate that the relative change in the transfer integral with respect to molecular displacement is $2 \text{ \AA}^{-1}$ [17].

4.1. $\text{MEM}_{1-x}\text{METM}_x\text{TCNQ}_2$

Fig. 4 shows the phase diagram of the $\text{MEM}_{1-x}\text{METM}_x\text{TCNQ}_2$ system [19,20]. The phase boundary is between the high-temperature phase, characterized by (almost) uniform chains and the low-temperature Peierls-distorted phase, which occurs for $x < 0.2$ only. The Peierls transition is suppressed for METM-TCNQ_2 , likely because the symmetry is already broken and a small gap is present in this case. The high-temperature phases are remarkably similar, the main difference being a doubled unit cell of METM-TCNQ_2 with respect to the MEM-TCNQ_2 unit cell. The METM -donor differs from MEM only by the replacement of the oxygen atom in the morpholinium ring by a sulfur atom. As a consequence the dipolar moments of both cations are different: 1.8 debye for MEM and 0.3 debye for METM [21]. For the mixed compound $\text{MEM}_{1-x}\text{METM}_x\text{TCNQ}_2$ this means that a random distribution of dipolar moment sizes produces a random distribution of Madelung energies on the TCNQ-sites. In MEM-TCNQ_2 the cations are free to perform a tumbling motion above 314 K [22]. The orientational disorder of the dipolar moments (and likewise the alteration of large and small dipolar moments) causes a disorder in the on-site energies of the TCNQ-molecules. The energy effect (δE) of a change in dipolar moment (δD) on the potential at a distance r is

$$\delta E \approx \frac{\delta D}{4\pi\epsilon_0 r^2}. \quad (4.1)$$

Fig. 4. Phase diagram of $\text{MEM}_{1-x}\text{METM}_x\text{TCNQ}_2$. The squares correspond to dimerization transition temperatures. D denotes the dimerized region.

The resulting potential disorder is for $\delta D \approx 1$ debye and $r \approx 7-10 \text{ \AA}$ of the order of a few tenths of an eV, which is large in comparison with the bandwidth, which is roughly 0.5 eV. Therefore it will localize the electron eigenstates and fill the gap (provided the gap is not too large). As mentioned above, the tumbling of the MEM-molecules takes place on a time scale that is very long compared to the time scale of electron motion (10^{-15} s) and therefore the electronic structure will be similar to a 1-D conductor with static dipolar disorder like Qn-TCNQ₂ [14].

With this information in mind, one sees that the α -values do indeed correlate with the disorder. The mixed compound MEM_{0.84}METM_{0.16}-TCNQ₂ has the lowest value for α (i.e. 0.15), corresponding to a completely flat distribution of pinning potentials. MEM-TCNQ₂ is disordered due to the reorientation of dipolar moments and has a somewhat higher α -value and METM-TCNQ₂ has no apparent disorder and has the highest value. Note that Qn-TCNQ₂, which should be similar to MEM-TCNQ₂ has indeed a comparable value of α . If MEM-TCNQ₂ is cooled below the dimerization transition temperature (340 K), a large gap is opened and the dipolar moments order and the non-linearities disappear.

The picture that emerges from the MEM_{1-x}METM_xTCNQ₂ system is corroborated by measurements on other systems within the morpholinium-TCNQ₂ class (see table 1). Systems with either a small gap or donor disorder display non-linearities, while strongly dimerized systems with ordered donor systems behave linearly. The fact that non-linearities do not (or hardly) occur in systems with a relatively large gap, may indicate that a finite density of states at Fermi-level is required to see these effects.

4.2. Dynamic disorder

Let us now consider METM-TCNQ₂. The donor system is perfectly ordered, while the form of the field and frequency dependent conductivity is not very different from disordered systems. The transfer integrals within the

TCNQ-chain are almost equal (0.178 and 0.177 eV [1]). The two equivalent TCNQ-sites have a slightly different Madelung energy ($E_1 - E_2 = 0.14 \text{ eV}$ [2]). In the rigid-lattice limit this leads to a band gap of 0.14 eV. However, at 300 K the vibrational amplitude of the TCNQ-molecules is roughly 0.2 $\text{\AA}$ [16], which combined with the estimate of the displacive dependence of the transfer integrals [17] leads to a dynamical spread of 30 to 40% in the values of the transfer integrals. A similar effect occurs for the local potentials. The derivative of eq. (4.1) with respect to displacement yields the appropriate energy change in this case

$$\delta E = \frac{\partial}{\partial r} \left(\frac{D}{4\pi\epsilon_0 r^2} \right) \cdot \delta r, \quad (4.2)$$

which will be of the order of 0.1 eV per $\text{\AA}$ displacement. With these parameters we are able to calculate the density of states (DOS) at 300 K for a finite, thermally disordered lattice in the same way as in [18]. The results are shown in fig. 5. Due to the thermal vibration of the anions, the gap has been filled with eigenstates, that are localized over 10–20 unit cells. This situation is quite analogous to Qn-TCNQ₂ which is considered as a disorder metal. It is relevant to note in this context that in $(\text{Et}_4\text{N})[\text{Ni}(\text{dmit})_2]$ and $(\text{Et}_4\text{N})_{0.5}[\text{Pd}(\text{dmit})_2]$, for which the concept of dynamical disorder was used to explain the temperature dependence of the conductivity [18],

Fig. 5. DOS of METM-TCNQ₂ in the rigid-lattice picture (dashed line) and for a thermally disordered lattice at 300 K (drawn line). The Fermi level is at zero energy

field dependences of the conductivity were seen that are similar to the ones discussed in this paper.

4.3. Anisotropy

As we have seen the non-ohmic behaviour is seen mainly when the electric field is directed along the TCNQ-chains. In the perpendicular directions the effect may be absent; in any case it is smaller by at least a factor 100. This effect can be explained using the concept of disorder in a quasi one-dimensional system: the localized wave-function in a 1-D disorder system is cigar-shaped, i.e. the localization length is much larger in the chain direction than in the perpendicular directions [23]. Within the theory of disorder, it is the voltage drop over a localization length that determines the onset of non-linear behaviour. This implies that the "onset" voltages are much larger in the directions perpendicular to the TCNQ-chain, in accordance with the experimental findings.

4.4. On the possibility of soliton transport in substituted morpholinium-TCNQ₂

As mentioned in the introduction, a puzzling phenomenon that accompanies charge transport in XY(T)M-TCNQ₂ is the shot noise contribution to the noise spectrum that was observed by Jos, Zijlstra and co-workers. In a series of papers they have argued that their measurements can best be understood if one assumes that the charge carriers are solitons with fractional charge $\frac{1}{2}$ [3–5]. Here we want to outline our objections against this picture, which was therefore not taken into consideration in the above discussion of the field and frequency dependence of the conductivity.

Following the work of Su, Schrieffer and Heeger [24, 25], who were the first to point out the importance of solitons in the Peierls condensed phase of a half-filled band system (polyacetylene), Rice and Mele [26] showed that in a (nearly) quarter-filled band system with large U , solitons with fractional charge $\pm \frac{1}{2}e$ may be formed. This idea was used by Jos et al. to

explain the shot noise component in the noise spectrum. Shot noise stems from carriers that cross the sample from one contact to the other ballistically (like in a vacuum diode). The resulting noise spectrum is a Lorentzian, its low-frequency level being directly related to the charge of the carriers. From these data Jos et al. conclude that the charge carriers have fractional charge $\pm \frac{1}{2}e$, although the experimental value of the charge quantum is in most cases somewhere between $\frac{1}{2}e$ and e . Within their model this observation is explained by assuming that part of the solitons bounce back from the contact and travel in the opposite directions as anti-solitons, thereby increasing the effective charge that is transported coherently [4].

The introduction of the soliton concept for the TCNQ-molecular stack as it was done for, e.g. the polyacetylene chain, is in our opinion not as straightforward as it seemed in the beginning. Solitons are topological excitations which may be present in a system with a degenerate ground state. The soliton is a bridge between two regions having a different realization of the ground state [27]. In the case of the Peierls condensate, the degenerate ground states are two different dimerization possibilities of the uniform chain (see fig. 6). In the case of M-TCNQ₂ however, the symmetry between the two realizations of the ground state is broken by the presence of the morpholinium molecule, i.e. there is only one form of the dimerization (one realization of the ground state) extending throughout the lattice. Furthermore, Jos et al. also apply their model to MEM-TCNQ₂ in the uniform phase [5], where

Fig. 6. (a) and (b) The two different ground states of a Peierls-dimerized system and (c) a soliton bridging between them.

they envisage a soliton that is decoupled from the lattice and that consists of a kink in the charge density wave in this system. Since the uniform phase is by definition undimerized and calculations indicate that the transfer integrals along the chain are equal to within 1% [1], in accordance with the metallic conduction that is found in this phase, this assumption seems hard to justify.

But even if one allows for the existence of a degenerate ground state, a mere application of the soliton concept as it was originally suggested for the explanation of the results of the noise measurements, is too simple. Supposing a soliton exists, which is coupled to the lattice, then it will always be coupled to neighbouring chains. Fig. 7 shows the propagation of a soliton, confined to one chain. As it propagates, the length over which there is a mismatch with the dimerization on neighbouring chains increases and thereby the energy associated with it. This leads to a friction term in the equation of motion for the soliton which exceeds the energy gain of soliton propagation in an electric field by many orders of magnitude. There are two ways to circumvent this problem:

- (1) Combine solitons on N different chains and let them propagate collectively. This reduces the mismatch effect and hence the "friction", relative to the energy gain resulting from the propagation of charged solitons in an electric field. However, in doing so the total charge that is transported coherently is now $\frac{1}{2}Ne$, which undermines the explanation of the noise measurements.
- (2) Form a soliton-antisoliton pair. In doing so

one has created an object which can move freely, its charge however is always an integer multiple of e .

Precisely the same argument has been given for crystalline polyacetylene. Whereas soliton transport is known to contribute to the electrical conductivity in amorphous polyacetylene [28], "in bulk crystalline material, interchain interactions should lift the degeneracy of the polymer's ground state, excluding the existence of moving solitons" [29]. Recently, elaborate calculations for crystalline polyacetylene have shown that solitons or polarons do not exist in the 3-D lattice structure [30].

Finally, we draw the attention of the reader to the fact that solitons are thought to play a part in the conduction process in $(\text{NMP})_x(\text{Phen})_{1-x}(\text{TCNQ})$ for $0.50 < x < 0.57$ [31]. In this system solitons are created when x is larger than 0.5. Even in such a system, soliton transport is relevant only at temperatures below 50 K. If we extend this argument to the morpholinium-TCNQ₂, a logical question is: why would the contribution of electrons be completely negligible? Especially for MEM-TCNQ₂, one expects a finite density of states at the Fermi-level, the contribution of which can certainly not be neglected.

In our opinion the measurements by Jos et al. are interesting and above all puzzling. Although soliton transport seems to give an explanation for the noise measurements the above considerations and the fact that the soliton picture has not been very helpful in understanding the field dependence of the conductivity [7] has led us to consider a different explanation.

Fig. 7. Two snapshots of a soliton propagating along a TCNQ-chain. The shaded areas indicate the regions of lattice mismatch among neighbouring chains.

5. Conclusion

We have shown that the electrical field and frequency dependences of the conductivity in XY(T)M-TCNQ₂ are consistently explained if one considers the system as effectively disordered. This may be either static or dynamic disorder. Also, the electron states may be localized by the temperature vibrations of the anions. The form of field and frequency dependence was found to be similar to that of Qn-TCNQ₂, in which disorder plays a crucial role. The empirical parameter α , which characterizes the form of the non-linearities is a measure of the degree of disorder of the electronic system.

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References

- [1] S. van Smaalen and J. Kommandeur, *Phys. Rev. B* 31 (1985) 8056.
- [2] S. Oostra, Ph.D. Thesis, Groningen University (1985).
- [3] H.F.F. Jos and R.J.J. Zijlstra, *J. Phys. C: Solid State Phys.* 25 (1986) L 62.
- [4] H.F.F. Jos, R.J.J. Zijlstra, J. Ike and I.J. Laurensse, *J. Phys. C: Solid State Phys.* 20 (1987) 3491.
- [5] H.F.F. Jos, R.J.J. Zijlstra, R.C.J. Vos and I.J. Laurensse, *J. Phys. C: Solid State Phys.* 20 (1987) 3511.
- [6] G.J. Kramer, J.L. Joppe, H.B. Brom, L.J. de Jongh and J.L. de Boer, *Synth. Metals* 19 (1987) 439.
- [7] H.F.F. Jos, Ph.D. Thesis, Utrecht (1986).
- [8] R.J.J. Visser, Th.W.L. van Heemstra and J.L. de Boer, *Mol. Cryst. Liq. Cryst.* 85 (1982) 265.
- [9] G. Grüner, *Physica D* 8 (1983) 1 and G. Grüner and A. Zettl, *Phys. Rep.* 119 (1985) 117.
- [10] K. Seeger, *Semiconductor Physics* (Springer, Berlin, 1985).
- [11] N.P. Ong and P. Monceau, *Phys. Rev. B* 16 (1979) 3443.
- [12] K.S. Cole and R.H. Cole, *J. Chem. Phys.* 9 (1941) 341.
- [13] G. Mihály, A. Jánosy, J. Kürti, L. Forró and G. Grüner, *Phys. Stat. Sol.(b)* 94 (1979) 287.
- [14] S. Alexander, J. Bernasconi, W.R. Schneider, R. Biller, W.G. Clark, G. Grüner, R. Orbach and A. Zettl, *Phys. Rev. B* 24 (1981) 7474.
- [15] B. van Bodegom, Ph.D. Thesis, Groningen University (1979).
- [16] R.J.J. Visser, Ph.D. Thesis, Groningen University (1984).
- [17] S. van Smaalen, J. Kommandeur and E.M. Conwell, *Phys. Rev. B* 33 (1986) 5378.
- [18] G.J. Kramer and H.B. Brom, *J. Phys. C: 21* (1988) 6085.
- [19] S. van Smaalen, J.L. de Boer, J. Kommandeur and G.J. Kramer, *Mol. Cryst. Liq. Cryst.* 120 (1985) 173.
- [20] G.J. Kramer, H.B. Brom, L.J. de Jongh and J.L. de Boer, *Festkörperprobleme XXV* (1985) 167.
- [21] G.J. Kramer, Theoretical dipolar moments, from a CNDO molecular orbital calculation, unpublished.
- [22] S. Oostra, B. van Bodegom, S. Huizinga, G.A. Sawatzky, G. Grüner and J.P. Travers, *Phys. Rev. B* 24 (1981) 5004.
- [23] G.J. Kramer and H.B. Brom, *Proc. of the ICSM'88, Santa Fe, Synth. Metals* 27 (1988) A133.
- [24] W.P. Su, J.R. Schrieffer and A.J. Heeger, *Phys. Rev. Lett.* 42 (1979) 1698.
- [25] W.P. Su, J.R. Schrieffer and A.J. Heeger, *Phys. Rev. B* 22 (1980) 2099.
- [26] M.J. Rice and E.J. Mele, *Phys. Rev. B* 25 (1982) 1339.
- [27] A.R. Bishop, J.A. Krumhansl and S.E. Trullinger, *Physica D* 1 (1980) 1.
- [28] A.J. Heeger (ed.), *Proc. of the ICSM'86, Kyoto, Synth. Metals* 17 (1987).
- [29] K. Holczer, C. Mathis and M. Ziliox, *Mol. Cryst. Liq. Cryst.* 117 (1985) 431.
- [30] P. Vogl, D.K. Campbell and O.F. Sankey, *Proc. of the ICSM'88, Santa Fe, Synth. Metals* 28 (1989) D513.
- [31] I.A. Howard and E.M. Conwell, *Phys. Rev. B* 29 (1984) 6879.