

Optical-phonon-mediated charge transport in substituted morpholinium TCNQ2 salts

Citation for published version (APA):

Kramer, G. J., Brom, H. B., & Jongh, de, L. J. (1986). Optical-phonon-mediated charge transport in substituted morpholinium TCNQ2 salts. *Physica B+C*, 143(1-3), 521-523. [https://doi.org/10.1016/0378-4363\(86\)90185-3](https://doi.org/10.1016/0378-4363(86)90185-3)

DOI:

[10.1016/0378-4363\(86\)90185-3](https://doi.org/10.1016/0378-4363(86)90185-3)

Document status and date:

Published: 01/01/1986

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

OPTICAL-PHONON-MEDIATED CHARGE TRANSPORT IN SUBSTITUTED MORPHOLINIUM TCNQ₂ SALTS

G.J. KRAMER, H.B. BROM AND L.J. DE JONGH

Kamerlingh Onnes Laboratorium, Rijksuniversiteit te Leiden, Postbus 9506, 2300 RA Leiden
 The Netherlands

Substituted morpholinium TCNQ₂ compounds exhibit some universal features with respect to the field, frequency and temperature dependence of the conductivity. These characteristics are different from the closely related morpholinium TCNQ₁ compounds. We show that a natural way to account for these phenomena comes about by careful examination of the order parameter space, i.e. the space created by the two different order parameters which together determine the gap at the Fermi surface: (i) the regular Peierls dimerization of the acceptor-acceptor overlap and (ii) a coherent shift of the donor molecules with respect to the acceptors. By describing small revolutions through parameter space (realized by phase coupling of two different phonons producing the above mentioned gap) the ground state electron gas is shifted with respect to the lattice, thereby producing a current. The model allows for a qualitative description of conductivity-related phenomena in these systems.

1. INTRODUCTION AND EXPERIMENTAL

The class of TCNQ compounds with substituted morpholinium as donor, has been extensively studied over the past decade, especially MEM(TCNQ)₂ which exhibits both a metal to semiconductor transition and a Spin-Peierls transition¹. In spite of this long-standing interest, the conductivity mechanism is still poorly understood. Below we present and discuss experiments on the dependence of the conductivity on both electric field strength and frequency. The latter type of experiments have proven to be useful in discriminating between conduction mechanisms in other 1-d compounds like NbSe₃ and Qn-TCNQ₂².

Figure 1 shows a typical example of the field and frequency dependence of a M-TCNQ₂ compound. Both experimental curves can be fitted to the same empirical formula

$$\sigma(x) = \sigma_0 \left(1 + A \cdot \exp\left[-x_m/x^\alpha\right] \right) \quad (1)$$

where x can be either electric field or frequency. For all compounds the temperature dependence of the conductivity is activated, with activation energies of the order of

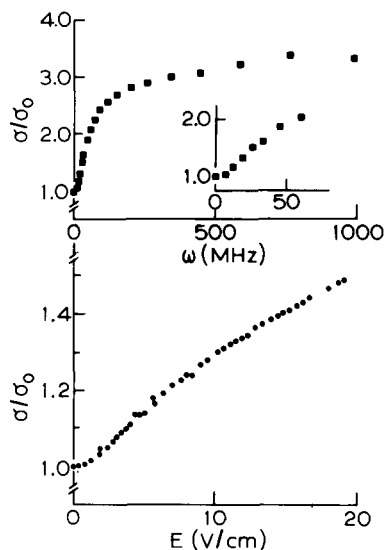


Fig. 1 Frequency and field dependence of the conductivity of methyl-ethyl-thiomorpholinium at room temperature. The insert shows the low-frequency data from which the similarity with the field-dependence is apparent.

0.1 eV. As regards the field-dependence we find that eq.(1) remains valid with temperature independent values for A , α and x_m , indicative of a single conductivity mechanism. The functional form of (1) shows - for $\alpha = 1$ - that the conductivity is in part activated in field and frequency. For all compounds which exhibit the above mentioned behaviour, the values for α were always markedly smaller than 1³. This can be explained by assuming a distribution in x_m . Indeed, it was found⁴ that the value of α can be related to the amount of disorder in the donor system. However, even for systems with a perfectly regular donor- and TCNQ-lattice, values as low as 0.5 were found for α . Another important observation is the absence of any such effects in compounds with a 1:1 donor to acceptor ratio.

Below we shall discuss a model for charge transport, which employs the unique features of charge transfer salts with 1:2 donor to acceptor ratio, and which provides for a qualitative understanding of our observations.

2. OPTICAL-PHONON-MEDIATED CHARGE TRANSPORT

In a charge transfer salt with 1:2 donor to acceptor ratio, the electron density at the Fermi-surface may be reduced by the deformation of the lattice with a periodicity of two TCNQ-spacings⁵. This can be done in two fundamentally different ways. Firstly, the TCNQ-spacing may alternate, which is the usual Peierls mechanism. Secondly, the donor molecules may undergo a $k=0$ shift with respect to the TCNQ-neighbours, resulting in an alternation of the energy of the TCNQ valence orbital, which gives rise to a gap at the Fermi-level and a modulated electron density with a periodicity of two TCNQ-spacings. The hamiltonian for the system reads:

$$\mathcal{H} = \sum_i [t + (-1)^i \tau] (C_{i+1}^+ C_i + C_{i+1} C_i^+) + \sum_i (-1)^i E C_i^+ C_i \quad (2)$$

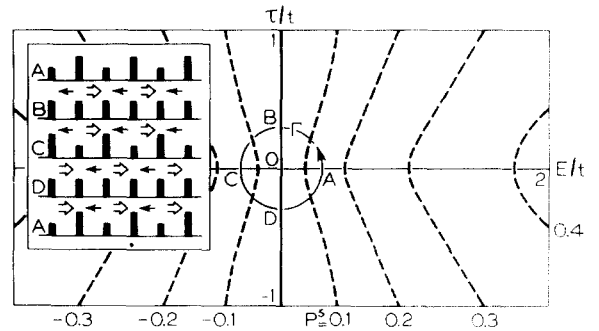


Fig. 2 Order parameter space for M-TCNQ₂ compounds. The dotted lines are contours of equal staggered electron density. The insert shows the changes in the ground state electron configuration resulting from proceeding along Γ . Fat (thin) arrows indicate large (small) overlaps.

where τ and E represent the mentioned deformations, which together span up a 2-dimensional order parameter space. Figure 2 shows this parameter space with the staggered electron occupation for the ground state, defined as

$$\rho^S = \frac{1}{2} + \rho_{2n} = \frac{1}{2} - \rho_{2n+1} \quad (3)$$

Fig. 2 is a good starting point for the formulation of the proposed charge transport mechanism. Let us assume the ground state electron gas to be governed by E and τ , and consider what happens upon passing along the trajectory ABCDA in fig. 2. The original staggered electron occupation diminishes at first along AB and then builds up again to a negative value over BC. All the way along ABC a net charge transport occurs from even- to the neighbouring odd-numbered sites. This transport has a left-right asymmetry since all the way along ABC, $\tau > 0$. Because the transition probability for an electron hop is proportional to the square of the overlap, this results in a net rightward charge transport, amounting to

$$\delta Q = \delta \rho^S (P(+)-P(-)) = \delta \rho^S \cdot 2\tau/t \quad (4)$$

As the reader may verify, the same rightward transport occurs in the second half of the loop (CDA) and hence

$$\delta Q = 2 \oint_{\Gamma} d\rho^s \frac{\tau}{t} \neq 0 \quad (5)$$

This implies that cooperative charge transport results from coherent variation of the two orderparameters E and τ . This in turn assures a coupling between the E - and τ -mode is coupled to the time dependence of the phase of the E -mode in such a way that charge is transported in the direction favoured by the electric field.

At this point we want to draw attention to the relation between the above proposed model and CDW transport in incommensurate 1-d metals. In the latter system, the slipping of the phase of the CDW order parameter allows for cooperative charge transport². In the present system a similar phase slip of either one of the order parameters alone would not contribute to the conductivity because of the high order of commensurability. As argued above, a joint, coherent modulation of both order parameters removes the objection of commensurability pinning by opening a new part of phase space. Another important difference is that in the commensurate system with two different order parameters, the total energy of the condensate is not - as for the regular CDW system - independent of the place on the circle in fig. 1. An inevitable consequence of our model is that in the M-TCNQ₂ system³, the contribution of cooperative charge transport is always temperature activated, in contrast to the idea of Fröhlich collective modes underlying the regular CDW system, which would give a contribution even at zero temperature.

From this the conclusion can be drawn that optical phonons should be responsible for the conductivity. Small, local fluctuations in the global value of the order parameters E and τ

are brought about by optical phonons. These fluctuations cause tiny revolutions in parameter space, which leads to cooperative charge transport. Consequently, the two different phonon modes get phase-coupled in the presence of an electric field⁶. This model does make some predictions for the electrical conductivity, which are indeed observed. Firstly, one finds a temperature activated conductivity. In the present treatment of the problem the activation energy is related to the optical phonon energies, which seems reasonable. Secondly, preliminary calculations for the field dependence of the conductivity yield both saturation at high fields and scaling of the field dependence with σ_0 , in accordance with the measurements⁴.

In conclusion: the model of optical-phonon-mediated charge transport, which specifically employs the unique structure of 1:2 donor-acceptor systems has been shown to account for some conductivity-related phenomena which can not be accounted for by "standard" models for 1-D conductors.

REFERENCES

1. S. Huizinga, J. Kommandeur, G.A. Sawatzky, K. Kopinga, W.M.J. de Jonge, Proc. Int. Conf. on Q1D Cond., Dubrovnik, 1978, Vol. 96 of Lecture Notes in Physics (Springer, Berlin, 1978), p.45.
2. G. Grüner and A. Zettl, Phys. Rep. 119, 117 (1985).
3. G.J. Kramer, J.L. Joppe, H.B. Brom, L.J. de Jongh and J.L. de Boer in the proceedings of the ICSM'86, to be published in Synth. Metals.
4. G.J. Kramer, H.B. Brom, L.J. de Jongh and J.L. de Boer, Festkörperprobleme, Advances in Solid State Physics XXV, 167 (1985).
5. We assume that the on-site electron-electron repulsion is much larger than the bandwidth, which is the case for M-TCNQ₂ compounds.
6. A detailed treatment can be found in G.J. Kramer, H.B. Brom and L.J. de Jongh, proceedings of the ICSM'86, to be published in Synth. Metals.