

Reply to comments on "Electrical transport properties of morpholinium-TCNQ2 compounds"

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REPLY TO COMMENTS ON “Electrical transport properties of morpholinium-TCNQ₂ compounds”

Physica B 167 (1990) 45

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Both in the work of Jos, and in our work, it is recognised that the conduction in all morpholinium-TCNQ₂ (MT₂) compounds has the same origin. While Jos argues in favor of solitons (in all systems), we argue against.

Instead of addressing Jos' comments one by one, the objections against the soliton picture emerge most clearly, by briefly recapitulating the soliton picture in transpolyacetylene (tPac) and thereafter considering the nature of the conjectured CDWs and solitons in the morpholinium-TCNQ₂ (MT₂) salts.

The concept of charged solitons in solid state physics is closely connected to tPac, where at low doping concentrations the susceptibility behaves peculiarly. Increase of the number of charge carriers (by doping) gives an initial decrease in the number of spin carriers.

The physics behind this phenomenon can most easily be illustrated with a free lying polymer with alternating single (A) and double (B) bonds with kinks separating the degenerate (ABAB..) and (BABA..) ground states. These kinks carry a spin, which under doping becomes compensated. Furthermore, it is calculated that there is only a small activation energy for moving such a kink (soliton) along the chain. At doping concentrations above a few percent the material becomes a band conductor [1]. Amorphous tPac contains approximately free lying chains. Still, in a recent analysis [2] it is shown that a single electronic defect can explain the dynamic nuclear polarization data, that were originally interpreted in terms of mobile and trapped solitons. In crystalline tPac even the existence of static solitons is questionable [3].

To recapitulate: in Pac mobile solitons might exist only in the amorphous trans-isomer (at low doping levels).

Let us now consider if such a soliton picture can be transferred to the MT₂ salts, as advocated by Jos et al. They present a picture of mobile solitons that are phase kinks in a CDW.

In all MT₂ compounds charge transfer between donor (morpholinium) and acceptor (TCNQ) is complete. This implies that the conduction band is quarter filled. Therefore, in the absence of incommensurate modulations, the “CDW” is commensurate with the lattice, manifesting itself in a crystallographic alternation of either TCNQ molecules or TCNQ–TCNQ bonds. Because of the asymmetric location of the morpholinium, which itself is an asymmetric molecule, the dimerisation of the TCNQ chain has only one realisation. This accords with the fact that all MT₂ systems (except MEMT₂) are dimerised at all temperatures. We can also phrase it differently: the CDW cannot (in

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general) be shifted over a half a unit cell, because the periodicity of the morpholinium system is equal to one unit cell.

If “domains” occurred, as suggested by Jos (point 3), these would actually be twinned crystals, rather than domains of a system with a twofold degenerate ground state. In this sense MT_2 is more alike cis-PAc, where the absence of degeneracy in the ground state hampers the realization of solitons.

For the type of MT_2 systems where solitons might still occur (high-temperature $MEMT_2$?), similar arguments as given above for crystalline polyacetylene are appropriate.

References

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