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THE 1-D HUBBARD MODEL WITH ALTERNATING CRYSTAL POTENTIAL
Comparision with experiments on DMM-$TCNQ_2$

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Abstract In this paper some properties are calculated of a quarter filled Hubbard band, where an extra term is added to the Hamiltonian, which describes the donor chain induced potential on the electron chain. Both exact and numerical results are presented. For DMM-$TCNQ_2$ we conclude that the potential difference between adjacent sites is approximately four times the transferintegral. At low temperature the magnetic exchange is observed to be strongly temperature dependent, for which a mechanism is suggested.

I. THE HAMILTONIAN

We introduce the following Hamiltonian

$$H = \sum_{i\sigma} t(c^{+}_{i+1\sigma}c_{i\sigma}+\text{h.c.}) + \sum_{i} Uc^{+}_{i\uparrow}c_{i\uparrow}c^{+}_{i\downarrow}c_{i\downarrow} + \sum_{i\sigma} E(-1)^{i}c^{+}_{i\sigma}c_{i\sigma} \qquad (1)$$

This is the Hubbard Hamiltonian to which a term is added which accounts for the Coulomb potential on the electron (TCNQ) chain, due to the donor chain[1]. For morpholinium-$TCNQ_2$ salts the Hubbard band is quarter filled. An exact treatment, which is possible only in the limits U=0 and U=∞, is given in section II. In section III we study the full Hamiltonian, using a finite chain approximation. Results of these calculations are applied to dimethylmorpholinium-$TCNQ_2$ (triclinic) in the last section.

II. LIMITING CASES U=0 AND U=∞

In the limits of zero and infinite correlation energy (U) Eq. (1) is reduced to

$$H = \sum_{i\sigma} t(c^{+}_{i+1\sigma}c_{i\sigma}+\text{h.c.}) + \sum_{i\sigma} E(-1)^{i}c^{+}_{i\sigma}c_{i\sigma} \qquad (2)$$

where $\sigma = \uparrow,\downarrow$ in the U=0 case and $\sigma = \uparrow$ for U=∞. Eq. (2) is diagonalized by a Fourier- and Bogoliubov transformation (this is done in ref 1. for another periodicity of the potential), yielding:

$$H = \sum_{k\sigma} (E^2+4t^2\cos^2 k)^{\frac{1}{2}}(\alpha^{+}_{k\sigma}\alpha_{k\sigma} - \beta^{+}_{k\sigma}\beta_{k\sigma}) \qquad (3)$$

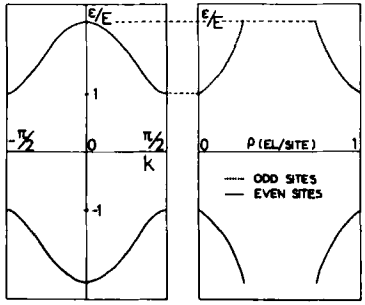


FIGURE 1 Pseudofermion spectrum (left) and charge distribution (right) for E/t=1.

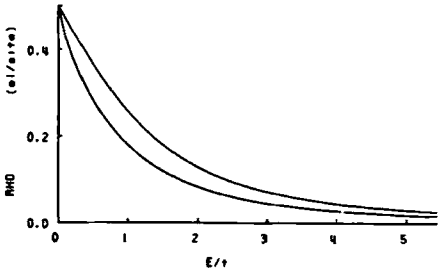


FIGURE 2 Groundstate charge distribution as a function of E/t for U=0 (upper curve) and U=∞ (lower curve).

The pseudofermion spectrum is given in FIG 1. The occupation ρ of odd and even sites for the α and β bands is then given by

$$\rho = \tfrac{1}{2}\left(1 \pm \frac{E}{(E^2+4t^2\cos^2 k)^{\frac{1}{2}}}\right) \qquad (4)$$

where the plus sign holds for (α,even) and (β,odd), and the minus sign otherwise. Using this formula the groundstate charge distribution is calculated, which is shown in FIG 2.

III. FINITE CHAIN CALCULATIONS

In order to treat the full Hamiltonian we choose a finite chain approximation. For a 4-site chain[2], for all possible electron occupation numbers (0-8) eigenvalues are calculated, thereby treating the problem within the grand canonical ensemble. This approach is supposed to give a better description of the infinite chain then a canonical appraoch, since one allows hopping between 4-site boxes[3]. The results of the calculatition can be summarized as follows:

-In the specific heat two anomalies occur. The low temperature one

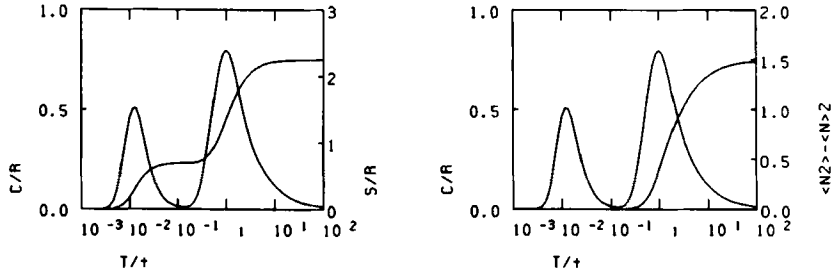


FIGURE 3 Finite chain results for U/t=6 and E/t=2 showing the nature of the two specific heat (C) anomalies. S denotes entropy.

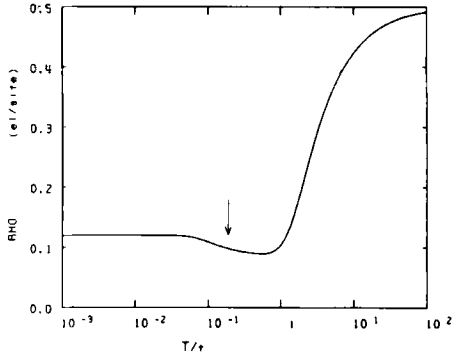


FIGURE 4 Typical temperature dependence of the charge distribution. The arrow denotes the value of J/t.

can be associated with antiferromagnetic short-range ordering (FIG 3), and one at T ~ t, indicative of an increasing electron mobility, as seen from the rise of the particle fluctuations within the boxes $\langle N^2\rangle-\langle N\rangle^2$ (FIG 3).

-The antiferromagnetic exchange J (which is, within our approximation, the singlet-triplet splitting), is found to be proportional to the product of electron occupations at adjacent sites. Furthermore, for U>>t, J is proportial to 1/U. Therefore:

$$J = \frac{4t^2\ \rho^{even}{}_x\ \rho^{odd}}{U} \qquad (5)$$

This results in a large E-dependence of the exchange ($J\propto 1/E^2$ for E>>t). For U/t=8 (which is applicable to DMM-$TCNQ_2$, see section IV) J drops an order of magnitude by varying E between 0 and 2.

-The charge distribution as a function of temperature has an extremum at nonzero temperature, that is for J<T<t (FIG. 4). We argue that this is not an artefact of our finite chain approximation, since it also occurs in the U=0 limit of the infinite chain (see FIG 1).

IV. DMM-TCNQ2 (triclinic)

IV.1 High temperature properties

Let us summarize the experimental data on DMM-TCNQ2:

-X-ray data show ρ(odd):rho(even)=0.85:0.15 [4].

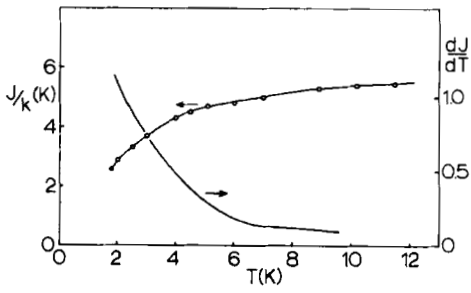
-The DC-conductivity shows a semiconductorlike behaviour, with gap Δ=0.58 eV.

-Magnetic susceptibility fits at high temperature to a Bonner-Fischer curve[5] with J/k =7K instead of 50-100K for other Morpholinium-$TCNQ_2$ compounds.

Furthermore the transferintegral has been calculated and is found to be 0.13 eV along the chain, which is two orders of magnitude larger then the interchain transferintegral, thereby establishing the one-dimensional character of the compound[5]. Since for TCNQ-salts U ~ 1 eV, we set U/t=8 in our calculations. All three experimental facts ensue a value of 2 for E/t.

IV.2 low temperature phenomena

It has been noted before that the susceptibility does neither fit to a Bonner-Fischer curve, nor to a Curie-Weiss law[5]. Since the one-dimensional nature of DMM-$TCNQ_2$ is not questionable, we fitted the susceptibility to the BF-curve, where J is temperature dependent (FIG 5). This accounts remarkebly well for the specific heat (FIG 6), for all temperatures above the 3-d ordering at 1.7 K. Although a temperature dependent exchange value seems to us the only plausible explanation of both specific heat and susceptibility measurements, the mechanism for such a change in J is a more difficult problem. On the bases of our finite chain calculations we would like to propose the following: at low temperature (T<t), J becomes temperature independent[6] and remains a function of U,E and t only. Also U is a constant and a $4k_F$-distortion of the TCNQ-chain has no driving mechainsm, since there is already a large gap at $4k_F$, due to the large E-value. Hence t is not likely to vary at low temperature. We therefore propose that the change in J is brought about by an increase in E. The driving mechanism would then be the minimalization of Coulomb interaction between donor and acceptor chain (E×ρ(even)-E×ρ(odd)), which is (for constant E) minimized at a temperature just above the exchange temperature (FIG 4).



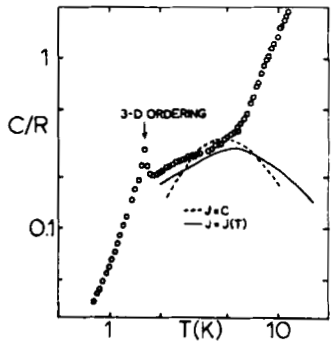


FIGURE 5 (left) Temperature dependent exchange value of DMM-$TCNQ_2$ as determined from susceptibility measurements.
FIGURE 6 (right) Specific heat of DMM-$TCNQ_2$. The dashed line is the spec. heat using J/k =5 K, the drawn line uses J(T) as determined from susceptibility (FIG. 6).

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